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ЖУРНАЛ АНАЛИТИЧЕСКОЙ ХИМИИ
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THE CHEMISTRY OF METALLIDES

By I. I. Kornilov

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Revised and edited by the author for the English edition.
Translated from Russian by J. W. Loweberg

The first book to deal comprehensively with the entire field of metallic compounds — metal-containing inorganic compounds other than salts — their formation, interaction, and relations between their behavior and the positions of constituent elements in the periodic system. Kornilov divides metallides into various classes and studies the reactions by analyzing equilibrium and property-composition diagrams of metallide component systems based on x-ray, microstructural, and physical-measurement data. Proceeding on the theory that continuous solid solutions can form in a metallide system only if the pure components have the same crystal structure, nearly the same lattice parameters, and the same type of chemical bonding, the work discusses binary, ternary, and higher systems of Kurnakov compounds, electron compounds, Laves phases, borides, silicides, carbides, nitrides, superconductor compounds, and semiconductors. Properties and applications (including rocket motors, crucibles for reactive materials, heat-resistant alloys, high-flux magnets, control rods and radiation absorbers for atomic reactors, photoresistors, transistors, thermoelectric elements, catalysts, etc.) of numerous heat-resistant, oxidation-resistant, semiconductive, and magnetic metallides and metallide systems are described. Unsolved problems in the field of metallide chemistry are discussed and extensive data on metallides are given in tables and diagrams.

CONTENTS: Metal Chemistry and Metallides: History of the subject • Definition of metal chemistry • Main factors determining the interaction of metals • **Metallides as Inorganic Compounds:** Classification of compounds according to Kurnakov • Kurnakov compounds • Berthollide-type compounds • Daltonide-type compounds • Strength and types of chemical bonding in metallides • Structure and compositions of metallides • **Reactions Between Metallides:** Methods of investigation • Main factors determining the interaction of metallides • Classification of ternary phases based on metallides • **Binary Metallide Systems with Continuous Solid Solutions:** Solid solutions of Kurnakov compounds • Solid solutions of compounds crystallizing from the liquid phase • Solid solutions of electron compounds • Solid solutions of nickel arsenide-type compounds • Solid solutions of Laves phase-type compounds • Solid solutions of $TiNi_3$-type metallides • Solid solutions of borides • Solid solutions of carbides • Solid solutions of silicides • Solid solutions of nitrides • Solid solutions of superconductor compounds • Solid solutions of semiconductor compounds • Other metallide systems with continuous solid solutions • **Binary Metallide Systems with Limited Solid Solutions:** Conditions limiting the continuous solubility of metallides • Examples of metallide systems with limited solubility • **Ternary and More Complex Systems • Some Properties of Metallides and Metallide Systems:** Characteristics of metallides in property — composition diagrams of metallic systems • Some properties of heat-resistant intermetallides • Some properties of semiconductor compounds • Magnetic properties of metallides • Oxidation resistance of refactory metallides in air • Strength properties of metallide systems • **Applications of Metallide Systems • Some Questions of Metallide Chemistry.**

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THE ANALYTICAL APPLICATIONS OF 8-MERCAPTOQUINOLINE (THIOOXINE) AND ITS DERIVATIVES

COMMUNICATION 10. THE RELATIVE STABILITY OF THIOOXINATES, AND THE EFFECT OF COMPLEXING AGENTS ON THE INTERACTION OF THIOOXINE WITH CATIONS*

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8-Mercaptoquinoline (thiooxine) forms with many elements intensely colored inner-complex salts which are soluble in organic solvents, and which are suitable for the photometric determination of a number of elements [1, 2]. The present article is devoted to a description of the results of a study of the relative stability of thiooxinates, and their behavior toward the action of complexing agents.

The stability series of thiooxinates. The relative stability of metal thiooxinates was determined in parallel by three methods based on: 1) substitution reactions; 2) the rate of formation of the thiooxinates, and 3) the extractability limits of the thiooxinates.

1. A chloroform solution of a thiooxinate was shaken for 1-2 minutes with excess of an aqueous solution of a cation, and, from the change in color of the chloroform layer, an assessment was made of the substitution of one metal by another in the thiooxinate. In the case of thiooxinates which were insoluble in chloroform or other organic solvents, tests for the substitution of one cation by another were carried out by the action of an aqueous solution of a salt of the cation on a solid thiooxinate which had been freshly prepared and carefully washed.

2. A solution of thiooxine dihydrate in an amount insufficient for complete binding of one of the cations was introduced into a test tube containing a solution of two metals in equal molar concentrations. The thiooxinate formed was extracted with chloroform, and, from the color of the extract, conclusions were made regarding the metal thiooxinate formed.

Both experimental variants were carried out in the same hydrogen-ion concentration range within which the complex formed has the highest stability.

3. The relative stability of the complexes can also be established on the basis of the extractability ranges in acid and alkaline solutions [1, 2] determined previously.

The following series was established for the thiooxinates on the basis of the experiments carried out:

$$Re > Au > Ag > Hg > Pd > Pt > Ru > Os > Mo > Cu > W > Cd >$$
$$In > Zn > Fe > Ir > V > Co > Ni > As > Sb > Sn > Bi > Pb > Mn > Tl.$$

This practical stability series of the thiooxinates is only a guide, since the methods given above do not always give similar results. The accurate position of certain individual elements can only be established after determining the dissociation constants of the thiooxinates of these elements.

*For communication 9, see Biokhimiya 23, 845 (1958). (See C.B. translation.)

Pilipenko [3] established a similar stability series for xanthogenates:

$$Hg^{II} > Hg^{I} > Au > Ag > Cu > Bi > Pb > Cd > Ni > Fe > Zn.$$

He showed that the xanthogenate series does not correspond completely to the sulfide series established by Tananaev [4] on the basis of the work of Bruner and Zawadsky [5]:

$$Au_2S_3 > HgS > Ag_2S > CuS > Bi_2S_3 > CdS > PbS > NiS > ZnS < FeS.$$

Complete coincidence with the sulfide series can only be expected in the case of the salts of mercaptans, thiophenols, and other HS-reagents which are incapable of inner-complex formation, since it is generally known that the stability of inner-complex salts depends on the stability of both the electrovalent and the coordination bonds. This is very clearly demonstrated in the interaction of thiooxinates with hydrogen sulfide. The experiments were carried out as follows. A chloroform solution of a thiooxinate was shaken in a test tube with an aqueous solution of H_2S adjusted to pH 1, pH 3, and pH 10. A control test with water (without H_2S) was carried out at the same pH. It is clear from Table 1 that only the sulfides of seven elements (Ag, Hg, Sb, Pb, As, Bi,

TABLE 1

Interaction of H_2S with Thiooxinates

Thio-oxinate	Reaction product of the thiooxinates with H_2S at various pH's		
	pH 1	pH 3	pH 10
Re	—	—	Na_2ReO_4 *
Au	—	—	—
Ag	Ag_2S	Ag_2S	Ag_2S
Hg	HgS	HgS	HgS
Pd	—	—	—
Pt	—	—	—
Ru	—	—	Partially decomposes
Os	—	—	—
Mo	—	—	—
Cu	—	—	—
W	—	—	Na_2WO_4 **
Cd	—	—	—
In	—	—	—
Zn	—	—	—
Fe	—	—	—
Ir	—	—	—
V	—	—	Decomposes***
Co	—	—	—
Ni	—	—	—
As	As_2S_3	Forms slowly As_2S_3	Na_3AsO_3
Sb	Sb_2S_3	Sb_2S_3	Sb_2S_3
Pb	PbS	PbS	PbS
Sn	—	—	—
Bi	Bi_2S_3	Bi_2S_3	Bi_2S_3
Mn	Decomposes	Partially decomposes	—
Tl	Tl_2S	Tl_2S	Tl_2S
Ta	—	—	Decomposes
Nb	—	—	Decomposes

*Decomposes to perrhenate.

**Decomposes to tungstate.

***Vanadate is formed in an alkaline medium in the presence of an oxidizing agent.

and Tl) are more stable than the thiooxinates. Hg, Ag, and As have an exceptionally high affinity for sulfur and form very stable sulfides. Sb, Pb, Bi, and Tl form less stable sulfides, and still less stable thiooxinates, in view of their incapacity to form stable coordination bonds with the nitrogen of the pyridine ring in thiooxine. Gold sulfide Au_2S_3 [6] is more stable than the sulfides of silver and mercury, but, in contrast to the thiooxinates of

silver and mercury, gold thiooxinate is not decomposed by hydrogen sulfide because of the greater stability of the coordination bond Au ... N in this compound. Arsenic gives an exceptionally stable sulfide, but does not form a coordination bond at all with nitrogen, as a result of which arsenic thiooxinate is only stable in relatively weakly acid solutions. On the other hand, zinc forms a sulfide which is only relatively slightly stable, but, thanks to the capacity of zinc to form amines and coordination bonds with nitrogen, the thiooxinate of zinc is appreciably more stable than its sulfide. In general, the last members of the stability series of the thiooxinates, namely As, Sb, Sn, Bi, Pb, Mn, and Tl, do not form any sort of stable amines and coordination bonds with nitrogen, as a result of which their thiooxinates exhibit poor stability. Meanwhile, the stability of the thiooxinates in the series As, Sb, Sn, Bi, Pb, Mn, and Tl, in general, drops in the direction of a decrease in the stability of the sulfides. The last member of the series (the thiooxinate of univalent thallium) is appreciably hydrolyzed by water, and, in certain properties, already approximates the properties of the alkali metal thiooxinates.

Rhenium, palladium, gold, copper, silver, and mercury form stable sulfides, and, at the same time, form compounds with a stable coordination bond with nitrogen. Accordingly, their thiooxinates exhibit a high stability. This is in agreement with Kuznetsov's views [7]. In general, one has the impression that the sulfides are appreciably more stable than the mercaptides (salts of reagents of the type R-SH), when no inner complex formation occurs.

The Relative Stability of Oxinates and Thiooxinates

Thiooxine belongs to the class of reagents of type R-SH, while oxine belongs to the type R-OH. All the same, in connection with the similarity in the structure of the inner-complex salts formed by thiooxine and oxine, it was of interest to establish the relative stability of oxinates and thiooxinates in various media. For this purpose, a solution of an oxinate in chloroform was shaken with an aqueous solution of thiooxine at pH 1-2 and at pH 10. From the changes in the color of the chloroform layer, conclusions were then made regarding the

TABLE 2

Relative Stability of Oxinates and Thiooxinates at pH 1-2 and pH 10

Cation	pH 1 — 2		pH 10		Cation	pH 1—2		pH 10	
	oxinate	thiooxinate	oxinate	thiooxinate		oxinate	thiooxinate	oxinate	thiooxinate
Re	—	+	—	+	Fe	—	+	+	+
Au	—	+	—	+	Ir	—	+	—	+
Ag	—	+	—	+	V	+	—	—	—
Hg	—	+	—	+	Co	—	+	—	+
Pd	—	+	—	+	Ni	—	+	—	+
Pt	—	+	—	+	As	—	+	—	+
Ru	—	+	—	+	Sb	—	+	—	+
Os	—	+	—	+	Sn	—	+	—	+
Mo	—	—	—	—	Bi	—	+	—	+
Cu	—	+	—	+	Pb	—	+	—	+
W	—	—	—	—	Mn	—	+ (pH 6)	—	+
Cd	—	+	—	+	Tl	—	—	—	+
In	—	+	—	+	Ta *	—	+	+	—
Zn	—	+	—	+	Nb *	—	+	+	—

*Ta and Nb only react with thiooxine in strongly acid media at a high thiooxine concentration.

relative stability of the oxinates or thiooxinates. In those cases where this experimental variant did not give decisive results or where the variant could not be carried out at all, excess of an alcoholic solution of a mixture of oxine and thiooxine in equimolar concentrations was added to an aqueous solution of the metal with a definite pH. The reaction product was extracted with chloroform, the color of which was then used to decide whether an oxinate or a thiooxinate had been formed. The results of these experiments are given in Table 2.

As is evident from Table 2, with the exception of vanadium (in acid media), and, presumably, tantalum

and niobium (in alkaline media), the thiooxinates of all the other elements are more stable than the oxinates. In an alkaline medium the oxinate and thiooxinate of iron have, apparently, similar stability.

The Effect of Certain Masking Agents on the Interaction of Thiooxine with Cations

The stability of thiooxine salts depends to a very large extent on the concentration (excess) of thiooxine in solution, as a result of which the completeness of formation of the complexes can be controlled by changing the thiooxine concentration, and also by varying the acidity of the medium. Of essential importance is the fact that the stability of the thiooxinates of various elements changes to very different extents when the thiooxine concentration and the acidity of the solution are changed by the same amount. As shown in the work we have carried out, the reason for this appears to be the complexing action of hydrochloric acid (at sufficiently high concentrations), which is manifested to very different extents for the various elements.

Hydrochloric acid at high concentrations is a strong masking agent. This is particularly clearly shown in the following examples. As mentioned above, silver and mercury form very stable complexes with thiooxine, and, even in 30 N H_2SO_4, can be detected at a dilution of 1:50,000. At the same time, in 10 N HCl, mercury and silver are complexed into such stable complexes that they do not react with thiooxine even when the concentration of the latter is 10 mg/ml. Hydrochloric acid in sufficiently high concentrations will also complex iron, antimony, bismuth, cadmium, tin, and other elements. By increasing the HCl concentration it is possible to mask ever-increasing amounts of the elements mentioned above. For example, in 6 N HCl, it is possible to mask 80 mg of Fe^{3+} in a volume of 50 ml, and it would seem that it should be possible, by increasing the HCl concentration further, to mask even greater amounts of iron. However, quite unexpectedly, it was found that in 10 N HCl, iron, when only present in relatively small amounts (5-6 mg), passes into the chloroform extract in the form of a pale-yellow complex, when the normal thiooxinate of iron has an intensely red-brown color. It is obvious that in 10 N HCl, the chloride complex anions of iron $FeCl_4^-$ or $FeCl_6^{3-}$ become very stable, and, as a result of the formation of simple salts of these anions with thiooxine (e.g., $C_9H_6NSH \cdot H_3FeCl_6$), the iron is extracted with chloroform. That thiooxine is a component of the salts extracted is proved by the fact that, on shaking the extract with water or ammonia, the extract is colored an intense red-brown – as a result of the hydrolysis of the chloride complex and the formation of iron thiooxinate with a normal composition $Fe(C_9H_6NS)_2$.

Bi^{3+}, Sn^{IV}, As^{III} behave similarly at high hydrochloric acid concentrations (6-10 N); this usually leads to low results for the test element because of the saturation of the extractant with weakly colored salts formed between thiooxine and the chloride anions of the elements mentioned, this is particularly true when chloroform is the extractant. These complexes are only extracted to a weak extent by other solvents. The fact that appreciable amounts of thiooxine are complexed to give such complex compounds may also be responsible for the low results obtained. This is the case in 10 N HCl during the determination of rhenium in the presence of large amounts of molybdenum, tungsten, and tin (see [8]).

Thus, formation of stable chloride anions of the elements which complex thiooxine in a hydrochloric acid medium, can lead, in certain cases, to complications. Such phenomena are not observed in sulfuric acid media, but, in the latter, the selective action of thiooxine is appreciably less. On the other hand, the chloride ions of hydrochloric acid are capable of partially substituting hydrogen ions in such stable anions as molybdate, tungstate, perrhenate, and some others. As a result of the probable transfer during this process of the elements from an anionic to a cationic form, it becomes possible to realize a quantitative interaction of thiooxine with the elements mentioned in strongly acid solutions. For example, perrhenate ions interact quantitatively with thiooxine in 5-10 N HCl. At the same time, this reaction only proceeds partially in sulfuric acid, whatever the concentration of the latter.

Sodium fluoride is an outstanding masking agent for trivalent iron and quadrivalent tin in solutions which are not too acid. At pH 2-5 it is possible to mask 50-100 mg Fe^{3+} in a volume of 50 ml. At higher acidities, e.g., 0.5-2 N HCl, the fluoride complex of iron, as is well known, is unstable because of the competitive action of chloride ions. It would seem that masking of iron should not cease to be effective, but, nevertheless, in 2-2.5 N HCl (even in the presence of a large amount of fluoride), it is already difficult to mask 15-20 mg of iron. On increasing the HCl concentration further, the chloro complex becomes very stable, and in 6 N HCl it is possible to mask 80 mg of iron. The same is true of Sn^{IV}, the fluoride complex of which at high HCl concentrations changes into the chloride complex, which also does not react under these conditions with thiooxine. The other elements are not masked by sodium fluoride.

Thiourea efficiently masks Cu, Ag, Au, Hg, Os, Ru, and Pt in strongly acid solutions, but only weakly masks Pd. The efficiency of the action of thiourea increases with increasing acidity of the solution and increasing thiourea concentration. This is extremely important, since it masks the majority of the very elements which form the most stable thiooxinates. In relatively weakly acid solutions (e.g., at a pH of about 1) the masking action of thiourea is manifested to a very weak extent. In 6 N HCl, however, it is possible, in practice, to mask Cu, Os, and Ru in amounts of several mg, and to mask 50 mg of Hg, and about 10-20 mg of Ag, Au, and Pt. Antimony, bismuth, and other elements which form insufficiently stable thiourea complexes, are not masked by thiourea.

Potassium cyanide in alkaline solutions masks appreciable amounts of Fe, Cu, Ag, Au, Pt, Ru, Os, Ir, Ni, Co, Pd and Rh. Masking is carried out simply by adding excess KCN to weakly alkaline or ammoniacal solutions of the salts of the elements. Using such a technique, in a volume of 5 ml (plus 2 ml of 5% KCN) it is possible to mask 3 mg Ni, 50 mg Co, 20 mg Cu, 1 mg Pd, 10 mg Ir, 5-6 mg Os, Ru, and Pt, and 20-30 mg Ag and Au. Zinc, cadmium, and mercury are not masked by cyanide. The values given are only relative values, since the amount of the element masked depends on the KCN concentration of the solution. It is much more difficult to complex iron as a cyanide complex. The methods described in the literature for masking iron with cyanide [13] do not give the desired results when working with thiooxine, since, when such methods are used, the iron is only very incompletely converted into the hexacyanoferrate ion. We have found that by using ascorbic acid as a reducing agent, quantitative conversion of the iron cation into the hexacyanoferrate ion proceeds at a pH of not higher than 9-10. When such a technique is used, it is possible to mask 5 mg of Fe^{II} in 15-20 ml of solution.

Potassium thiocyanate in strong excess in an acid medium (pH 1-3) is a strong masking agent for trivalent iron. In the presence of thiooxine, when large amounts of iron are present, a crystalline raspberry-red precipitate is formed, which is insoluble in $CHCl_3$, CCl_4, and C_6H_6, and is soluble in isoamyl acetate and other esters. It is similar to compounds described in the literature, which are formed in the presence of Fe^{III}, thiocyanates, and heavy organic bases such as pyramidone [9], urotropine [10], acridine [11], or naphthylamine [12].

Cadmium and zinc at very high KSCN concentrations in solution (about 20%) do not react with thiooxine, but when high concentrations of Cd and Zn are involved, yellow crystalline precipitates separate out which are formed by the cation of thiooxine and the thiocyanate anions of zinc or cadmium. These precipitates, which are pale yellow in color, are soluble in chloroform. Mercury, antimony, bismuth, cobalt, the platinum metals, and other metals are not masked by potassium thiocyanate.

Potassium iodide masks bismuth and cadmium. When these elements are present in appreciable concentrations, crystalline precipitates formed between the iodide-complex anions and the thiooxine cation may separate out. Sb, Zn, and Hg, and other elements are not masked by iodide.

Phosphoric acid does not mask any of the test elements. Only a few tenths of a gram of trivalent iron can be masked by a concentrated solution of phosphoric acid.

Oxalic acid masks milligram amounts of divalent iron, tungsten, and vanadium. Other elements are not masked.

Ammonia does not firmly mask relatively small amounts of cobalt. Ammonia does not mask the remaining elements.

Tartaric acid in acid media masks moderate amounts of tungsten. Alkali solutions of tartaric and other hydroxy acids do not affect the interaction of thiooxine with other cations.

All that has been said relates to cases where a large excess of thiooxine is used in comparison with the concentration of the cations. When only a small excess of thiooxine is used, presumably, many weaker complexing agents will exhibit an appreciable masking effect.

SUMMARY

A stability series has been established for the thiooxinates of 26 elements. It has been shown that the stability of the thiooxinates depends not only on the bond metal–sulfur, but to a considerable extent on the stability of the bond metal–nitrogen.

In acid and alkali media, the thiooxinates of elements which form sulfides which are not hydrolyzed by water, are more stable than the oxinates, with the exception of those of vanadium (in acid solutions), and niobium and tantalum (in alkaline solutions).

When thiooxine is used for analytical purposes, the most powerful masking agents are: high concentrations of hydrochloric acid (for Fe, Mo, Hg, Ag, Bi, Sn, and Sb), thiourea (Cu, Ag, Au, Pt, Hg, Ru, and Os), and sodium fluoride (for Fe^{III} and Sn^{IV}), and, in alkaline solution, potassium cyanide (Fe^{2+}, Ag, Au, Pt, Ru, Os, Ir, Pd, Ni, and Co). Potassium thiocyanate is a good masking agent for Fe^{III} and moderate amounts of Zn and Cd.

LITERATURE CITED

[1] Yu.A. Bankovskii, Latvijas PSR Zinatnu Akademijas Vestis 9, 111 (1952).

[2] V.L Kuznetsov, Yu.A. Bankovskii, and A.F. Ievin'sh, Zhur. Anal. Khim. 13, 267 (1958).*

[3] A.T. Pilipenko, Zhur. Anal. Khim. 4, 227 (1949).

[4] A.N. Tananaev, Uspekhi Khim. 10, 621 (1941).

[5] L. Bruner and J. Zawadsky, Z. anorg. Chem. 65, 136 (1910).

[6] G.A. Medvedeva, Zhur. Anal. Khim. 3, 103 (1948).

[7] V.L Kuznetsov, Zhur. Anal. Khim. 6, 140 (1951); 2, 73 (1947).

[8] Yu.A. Bankovskii, A.F. Ievin'sh, and Z.E. Liepinya, Izvest. Akad. Nauk Lat. SSR 11 (136), 129 (1958).

[9] A. Martini, Mikrochem. 16, 223 (1928).

[10] A. Martini, Mikrochem. 6, 28 (1928).

[11] A. Martini, Mikrochem. 8, 143 (1930).

[12] R. Berg, J. prakt. Chem. 115, 178 (1927); R. Berg and O. Wurm, Ber. 60, 1664 (1927).

[13] R. Berg, The Use of o-Hydroxyquinoline in Analytical Chemistry [in Russian] (ONTI, Moscow, 1937).

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A POTENTIOMETRIC STUDY OF THE FORMATION OF MIXED URANYL AND ALKALI METAL FERROCYANIDES

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The reaction between uranyl salts and the ferrocyanides of the alkali metals has been known for a long time, but it has been studied to a comparatively small extent, although it is often used as a proof of the presence of uranyl ions in solution, the ferrocyanide used for this purpose being almost invariably potassium ferrocyanide. The published data on the composition of the precipitate formed thereby is contradictory. The question is complicated further by the fact that the composition of sparingly soluble ferrocyanides, as a number of workers have shown [1-3], depends on the nature of the univalent cations present in solution.

The published literature is devoted mainly to the composition of the uranyl ferrocyanide obtained on precipitating with potassium ferrocyanide; the following formulas, e.g., have been attributed to the compound thereby formed: $(UO_2)_2R$* [4]; K_2UO_2R [5]; $K_2UO_2R_xUO_2(NO_3)_2$, while in concentrated solutions there is a tendency for the following compounds to be formed: K_2UO_2R [6]; $K_4(UO_2)_4R_3$ [7, 3]; $K_{12}(UO_2)_8R_7$ is formed in the presence of excess K^+ ions [3].

There is less information on the composition of the uranyl ferrocyanide formed on precipitation with the ferrocyanides of the other alkali metals. The following formulas have been ascribed to the precipitates obtained with sodium ferrocyanide: $(UO_2)R_2$ [3]; $5(UO_2)_2R \cdot Na_4R$ and $5(UO_2)_2 \cdot R2Na_4R$** [8], while to the precipitates obtained with rubidium and cesium ferrocyanides the following formula has been ascribed: $M_4(UO_2)_4R_3$, where M = Rb, Cs [3].

Preparative methods and the solubility method have been used in the main in the papers cited; only individual results have been obtained by a potentiometric method. A study of the composition of the mixed ferrocyanides of copper [9] has, however, shown that the potentiometric method is fully applicable, and is very convenient for establishing the composition of mixed ferrocyanides, particularly in view of the fact that uranyl ferrocyanide is very easily peptized and leads to considerable difficulties when other research methods are used.

The present article is devoted to results obtained during a study of the interactions which occur in the system $UO_2^{2+} - M_4R - H_2O$, where M = Li, Na, K, Rb, and Cs.

The oxidation-reduction potential was determined on a LP-5 potentiometer using a platinum indicator electrode and a saturated calomel electrode.

Preliminary experiments were carried out on the potentiometric titration of solutions of uranyl nitrate with potassium ferrocyanide in order to establish the concentrations of the solutions, and the conditions under which the oxidation-reduction potential falls most sharply. It was established that only at comparatively high concentrations of the uranyl salt and of potassium ferrocyanide is there observed on the oxidation-reduction potential curves a characteristic break, which makes it possible to establish the composition of the mixed ferrocyanide of uranyl and alkali metal; sloping curves are obtained when low concentrations are used. A clearly defined break is obtained on introducing a comparatively large amount of ferrocyanide; preferably, the ferrocyanide should be added to the uranyl salt being titrated, rather than the other way around. The concentration of the working solutions of M_4R, M_3R, and $UO_2(NO_3)_2$ was about 0.1-0.2 mole/liter. During titration, 0.3 ml of ferrocyanide was

*Here and henceforth R designates $[Fe(CN)_6]$.

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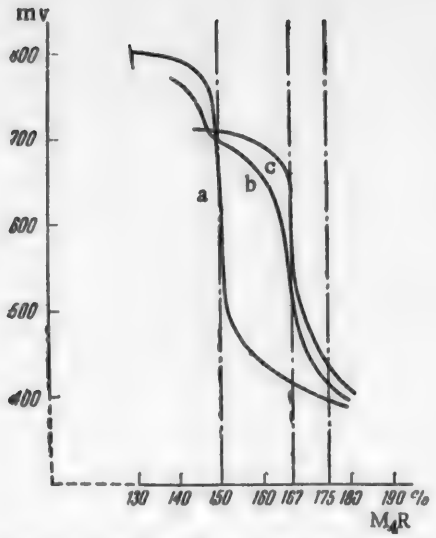


Fig. 1. Changes in the oxidation-reduction potential during titration of $UO_2(NO_3)_2$ with the following solutions: a) K_4R; b) K_4R + RbCl; c) K_4R + CsCl.

added to 10 ml of uranyl nitrate solution, and the volume of the solution made up to 50 ml. The solution was carefully agitated during titration.

In order to establish the relation between the composition of the precipitate and the nature of the alkali metal present in solution, the original solution of $UO_2(NO_3)_2$ was titrated with solutions of the ferrocyanides of potassium, sodium, and lithium, to which, in separate experiments, the following salts were added in equivalent amounts: RbCl or CsCl; KCl, RbCl, or CsCl; NaCl, KCl, RbCl, or CsCl. Twelve titrating solutions were thereby used.

Solutions of sodium and lithium ferrocyanides were prepared from potassium ferrocyanide via lead ferrocyanide [9]. Sodium and lithium ferricyanides were prepared by oxidation of the corresponding ferrocyanides with chlorine water.

On the basis of the experimental results obtained, diagrams were constructed in which the amount of the alkali metal ferrocyanide (expressed as a percentage of the amount necessary for forming normal uranyl ferrocyanide) was plotted along the abscissa, while the oxidation-reduction potentials were plotted along the ordinate.

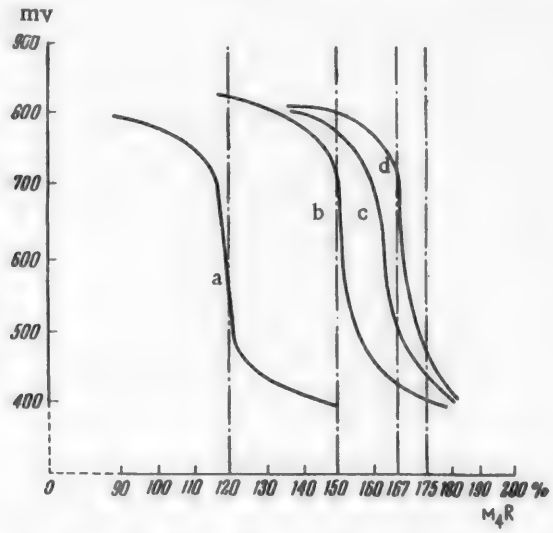


Fig. 2. Changes in the oxidation-reduction potential during titration of $UO_2(NO_3)_2$ with the following solutions: a) Na_4R; b) Na_4R + KCl; c) Na_4R + RbCl; d) Na_4R + CsCl.

The curves depicting changes in the oxidation-reduction potential during titration with potassium ferrocyanide are shown in Fig. 1. The most rapid drop in the oxidation-reduction potential is observed when, of the alkali metals, only potassium ions are present in solution, while the break in the curve is observed on addition of 149-150% of ferrocyanide (a). When titration is carried out with potassium ferrocyanide to which an equivalent amount of rubidium chloride has been added, the break on the curve (b) occurs at 167-168% ferrocyanide, while on addition of an equivalent amount of cesium chloride, the break occurs at 166-167% (c).

The change in oxidation-reduction potential during titration with sodium ferrocyanide is shown in Fig. 2. When only sodium ions are present, the break is observed on addition of 117-120% ferrocyanide (a). When titra-

tion is carried out with sodium ferrocyanide to which an equivalent amount of potassium chloride has been added, the break on the curve (b) is observed at 149-150%, i.e., on addition of the same amount of sodium ferrocyanide as in the titration with potassium ferrocyanide. When rubidium chloride (c) and cesium chloride (d) are added to the sodium ferrocyanide solution, the breaks on the curves are observed on addition of 164-165% and 166-167% of ferrocyanide.

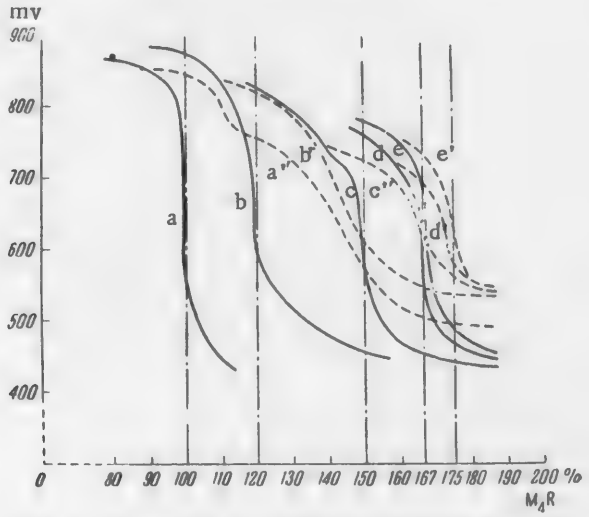


Fig. 3. Changes in the oxidation-reduction potential during titration of $UO_2(NO_3)_2$ with the following solutions: a) Li_4R; a') Li_4R + LiCl; b and b') Li_4R + NaCl; c and c') Li_4R + KCl; d and d') Li_4R + RbCl; e and e') Li_4R + CsCl.

The curves shown in Fig. 3 were constructed on the basis of the results obtained during titration with lithium ferrocyanide. When only lithium ions are present, the break on the oxidation-reduction potential curve (a) is observed on addition of 99-101% of ferrocyanide. During titration with lithium ferrocyanide in the presence of the ions of the other alkali metals, the same regularities are observed in the values of the oxidation-reduction potentials as during titration with sodium and potassium ferrocyanides. Thus, on titrating with lithium ferrocyanide solutions to which sodium chloride (b), potassium chloride (c), rubidium chloride (d), and cesium chloride (e) have been added in equivalent amounts, the breaks are observed on the curves at 118-120%, 149-150%, and 166-167% and 167-168% of ferrocyanide.

From the character of the curves for the oxidation-reduction potentials and the position of the breaks it can be concluded that during precipitation of uranyl salts with lithium ferrocyanide, normal uranyl ferrocyanide is formed: $(UO_2)_2R$.

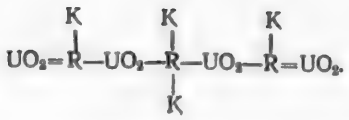
During precipitation of the salts with sodium or lithium ferrocyanides in the presence of sodium ions introduced in an equivalent amount to the amount of lithium, presumably a mixed ferrocyanide of uranyl and sodium is formed $5(UO_2)_2R \cdot Na_4R$ or $Na_2(UO_2)_5R_3$. The structure of this salt can be depicted as follows:

$$UO_2{=}\overset{\displaystyle Na}{\overset{|}{R}}{-}UO_2{-}\overset{\displaystyle UO_2}{\overset{\|}{R}}{-}UO_2{-}\overset{\displaystyle Na}{\overset{|}{R}}{=}UO_2.$$

When potassium ferrocyanide, or lithium and sodium ferrocyanides in the presence of an equivalent amount of potassium, are added to a solution of an uranyl salt, then a mixed ferrocyanide of uranyl and potassium is formed

$$2(UO_2)_2R \cdot K_4R,$$

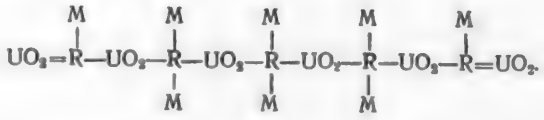
or, in another form



During the interaction of uranyl salts with the ferrocyanides of the alkali metals in the presence of rubidium and cesium ions, when the latter are added in equivalent amounts to those of lithium, sodium, or potassium, the break on the curves corresponds to the formation of mixed ferrocyanides of the type

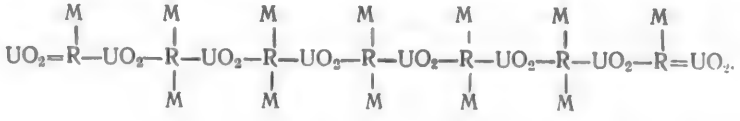
$$3(UO_2)_2R \cdot 2M_4R,$$

or, in another form



Excess of alkali metal ions affect the results of potentiometric analysis strongly: the potential drop becomes less sharp, and the curve is shifted toward formation of mixed ferrocyanides containing a large amount of the alkali metals.

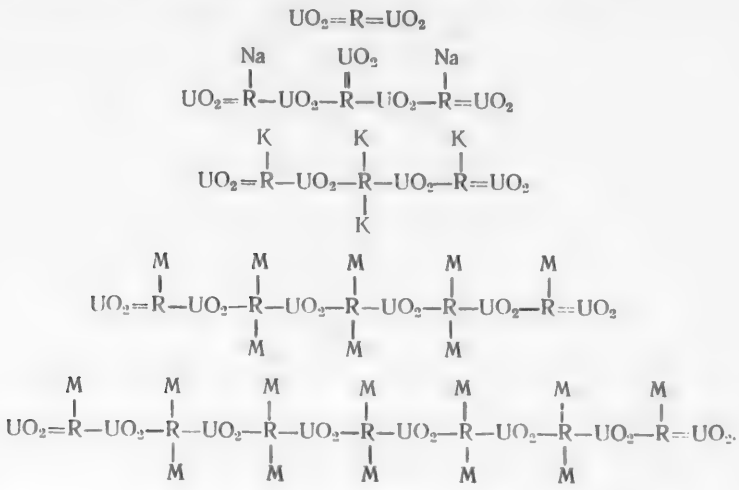
It should be pointed out that the shift in the break on the oxidation-reduction potential curve in the presence of excess alkali metal ions complicates the use of the potentiometric method for analytical purposes considerably. This is particularly clearly shown in Fig. 3, in which are shown the titration curves (a', b', c', d', and e') for uranyl nitrate with lithium ferrocyanide in the presence of a large excess of alkali metal ions. The alkali metal chlorides were added in these experiments to the uranyl nitrate solution in amounts such that the solutions were saturated with respect to the chlorides in all cases, with the exception of lithium chloride, which was added in an amount corresponding to a saturated solution of sodium chloride. It was established that, in the presence of large, excessive amounts of lithium, sodium, and potassium ions (a', b', and c') the oxidation-reduction potential curves do not exhibit sharp breaks, while,in the presence of rubidium and cesium ions (curves d' and e'), the break occurs at a point corresponding to 175% of ferrocyanide, the composition of the precipitates formed in this case corresponding to the formula: $4(UO_2)_2R \cdot 3M_4R$. It should be pointed out that, in this case, the volumes of the uranyl solutions containing excess rubidium and cesium that were taken were a tenth of those taken in other instances. Since the potentiometric titration curves obtained for solutions containing a large excess of Li^+, Na^+, and K^+, had a very sloping character without any clearly expressed breaks, determination of the compositions of the mixed uranyl ferrocyanides was carried out by titrating the excess of the alkali metal ferrocyanide with potassium permanganate in a strongly acid medium [10]. The ferrocyanides of K, Na, and Li were taken in amounts which were 3.5 times that theoretically required for the formation of normal uranyl ferrocyanide. The alkali metal chlorides were added in the amounts necessary for obtaining saturated solutions (apart from lithium chloride, which was taken in an amount corresponding to a saturated solution of sodium chloride). The mixed ferrocyanide of uranyl was then precipitated and the precipitate filtered off. Excess ferrocyanide in the filtrate was titrated with potassium permanganate. It was found that precipitates of the mixed ferrocyanides of uranyl with sodium and potassium correspond accurately to the formula: $4(UO_2)_2R \cdot 3M_4R$, while the mixed ferrocyanide of uranyl and lithium approximates to this composition. This formula can be represented structurally as follows:



The results obtained lead to the conclusion that the mixed ferrocyanides of uranyl and the alkali metals can be expressed by the general formula: $n(UO_2)_2 \cdot (n-1)M_4R$.

When M = Li, Na, K, Rb, and Cs, n assumes the values of 1, 1¼, 2, 3, and 3, respectively; in the presence of a large excess of Rb^+ and Cs^+, n = 4.

Structurally, the formulas can be represented as follows (M = Rb or Cs):



Thus, the mixed ferrocyanides of uranyl and the alkali metals, apparently, are polymeric molecules in which the number of units can be appreciable, depending on the conditions (in particular, on the nature of the alkali metal present in the molecule). The length of the chain of the polymeric molecules, apparently, increases with the atomic weight of the alkali metal, and tends, in the limit, to the composition M_2UO_2R, but does not reach this composition even under very "severe" conditions (a large excess of alkali metal ions). In the polymeric molecules adduced, the alkali metals will probably undergo exchange (as in the case of ion exchange on resins) in order of increasing bond stability from Li to Cs.

SUMMARY

It has been established that the position of the equivalence point, corresponding to a break on the oxidation-reduction potential curves, in the systems $UO_2^{2+} - M_4[Fe(CN)_6] - H_2O$ (M = Li, Na, K, Rb, Cs) depends on the nature of the alkali metal present in solution. When lithium ferrocyanide is present, a normal uranyl ferrocyanide is formed $(UO_2)_2[Fe(CN)_6]$. When the remaining alkali metals are present, mixed ferrocyanides are formed:

$$Na_2(UO_2)_5[Fe(CN)_6]_3;\ 2(UO_2)_2[Fe(CN)_6]K_4[Fe(CN)_6];$$
$$3(UO_2)_2[Fe(CN)_6]\cdot 2Rb_4[Fe(CN)_6];\ 3(UO_2)_2[Fe(CN)_6]\cdot 2Cs_4[Fe(CN)_6].$$

In the presence of excess alkali metal ions the equivalence point is shifted toward formation of compounds containing large amounts of the alkali metals, while in the presence of very high concentrations of the solutions of alkali metal chlorides, a mixed uranyl ferrocyanide is formed:

$$4(UO_2)_2[Fe(CN)_6]\cdot 3M_4[Fe(CN)_6].$$

It is suggested that the mixed uranyl ferrocyanides be regarded as polynuclear molecules of the polymer type.

LITERATURE CITED

[1] L.V. Tananaev and M.I. Levina, Zhur. Neorg. Khim. 2, 576 (1957).

[2] L.V. Tananaev and M.A. Glushkova, Zhur. Neorg. Khim. 2, 594 (1957).

[3] L.V. Tananaev and M.I. Levina, Zhur. Neorg. Khim. 3, 2045 (1958).

[4] F. Treadwell and V. Hall, Qualitative Analysis [Russian translation] (Goskhimizdat, Moscow, 1946).

[5] A. Noyes and V. Bray, Qualitative Analysis of Rare Elements [Russian translation] (ONTI, Moscow, 1936).

[6] J.N. Gaur, H.C. Gaur, and A.K. Bhattacharya, J. Ind. Chem. Soc. 30, 158, 163 (1953).

[7] V.G. Sochevanov, N.V. Shmakova, and G.A. Volkova, Zhur. Neorg. Khim. 2, 2049 (1957).

[8] G.A. Kleibs, Zhur. Neorg. Khim. 1, 2177 (1956).

[9] V.D. Ponomarev and I.V. Tananaev, Zhur. Anal. Khim. 13, 417 (1958).•

[10] I. Kolthoff, Volumetric Analysis [Russian translation] (Goskhimizdat, Moscow, 1932) vol. II, p. 288.

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SEPARATION OF CERTAIN ISOTOPES BY THE METHOD OF FOCUSING ION EXCHANGE

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Chromatography and electrochromatography have found application in recent years for separating fragments arising from the fission of heavy nuclei [1-4]. The duration of the experiment itself, which amounts to several hours, is a drawback of these methods. Of considerable interest is the search for new, more efficient methods of separation. Recently, a number of authors have suggested a new technique of electrophoretic separation of complex systems, in which a pH gradient, or a gradient in the concentration of complexing agents, is applied in parallel to the electric field. This technique has been used for separating both organic materials [5, 6] as well as inorganic ions [7-9]. The work described in the present article was carried out with the aim of studying the possibilities of using the method of focusing ion exchange for separating fission nucleides. We thought it would be of the greatest interest to follow the behavior of the rare earths, and to develop conditions for separating them from each other and from the alkaline earth elements.

The so-called method of focusing ion exchange has been described in a series of articles [5-9]. In a solution of a complexing agent which is capable of forming negatively charged ions with the ions of some elements, a mobile equilibrium is established between the various ionic forms. Let us imagine an extended (drawn out) capillary system, e.g., a sheet of filter paper in which, as a result of the transfer of the ions of a complexing agent in an electric field, a concentration gradient is established for this complexing agent. In such a case, in the region where there is a high concentration of the complexing agent, the negatively charged complex ions will predominate, while in the regions of low complexing agent concentration the cationic forms M^{n+} (Fig. 1) will dominate.

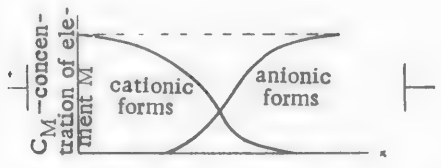

Fig. 1. Distribution of the ionic forms of an element M when a concentration gradient has been established for the complexing agent.

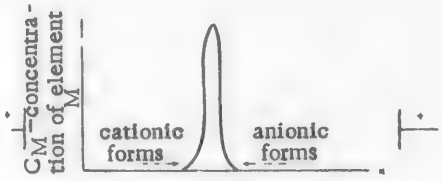

Fig. 2. Focusing process.

Under the action of an electric field, the negatively charged ions will move toward the anode, while the positively charged ions will move toward the cathode (Fig. 2).

As a result of this process, all the element M will be concentrated in a narrow zone. The position of this zone will be determined by the concentration gradient of the complexing agent, and also by the instability constant of the complexed ion.

If a mixture should contain several elements M_1, M_2, M_3, which give different complex compounds with the same complexing agent, and the instability constants of the complex anions formed are different, then a state of exchange equilibrium will be established between them. It is obvious that each of these elements will be concentrated in different places in accordance with their instability constants. Thus, it is possible that not only concentration will occur, but also separation of these elements.

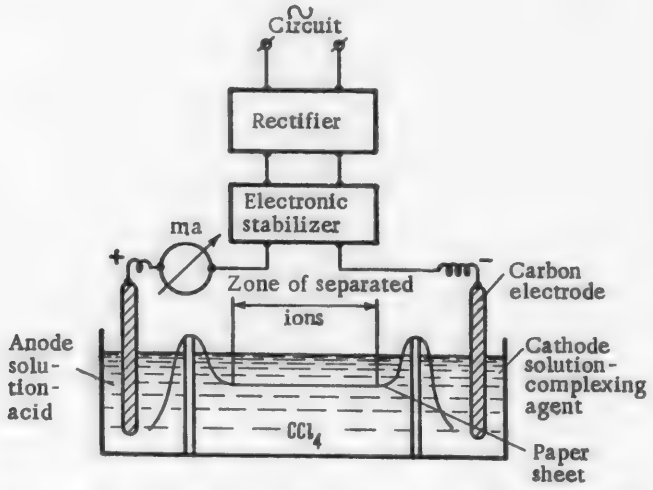

Fig. 3. Schematic diagram of the setup used for the separation.

The experimental setup is shown in Fig. 3.

First of all, lines are drawn with a pencil at intervals of 2-3 mm on a sheet of filter paper, then, on a certain part in the middle of the sheet, a few drops of the radioactive solution containing the isotopes to be separated is placed. The ends of the paper sheet dip into the electrode vessels, while the central part of the sheet is immersed in a vessel containing CCl_4. A current of 2-10 milliamp at a voltage of 260-280 volts (about 20-30 volts/cm) is then applied. In approximately 2-5 minutes, a concentration gradient is established, and, after another 2-3 minutes, the elements are separated and concentrated.

When the process is complete, the current becomes constant. Separation is usually complete in 5-10 min.

TABLE 1

Expt. No.	Cathode solution		Anode solution – hydrochloric acid	
	complexing agent	concentration complexing agent, M	pH	concentration M
1a	Sodium ethylene-diamine-tetracetate	0,1	11	0,5
1б	» »	0,01	11	0,5
2a	» »	0,1	11	0,5
2б	» »	0,1	11	0,1
2в	» »	0,1	11	0,02
3a	» »	0,1	11	0,5
3б	» »	0,1	7	0,5
3в	» »	0,1	4	0,5
4a	» »	0,1	7	0,5
4б	Citric acid	0,03	12	0,5

The position of the zones is found either by means of autoradiography, or directly, by measuring the activity of parts of the paper and mapping out the activity distribution.

The separated isotopes are identified from the half-life period or by determining the maximum energy of the β-radiation.

Separation of Sr and Y. The separation of Sr^{90} and Y^{90} without carriers was studied first. Solutions of citric acid and sodium ethylenediaminetetracetate were used as complexing agents.

The experimental conditions are given in Table 1.

Changing the concentration of sodium ethylenediaminetetracetate in the cathode solution from 0.1 to 0.01 M affects separation of Sr^{90} and Y^{90} insignificantly. Lowering the concentration of sodium ethylenediaminetetracetate to 0.01 M leads to poorer separation; however, the separation is still complete. Variations in the pH of the electrode solutions also have little effect on the separation of the given isotopes.

Compared with sodium ethylenediaminetetracetate, citric acid (under the given experimental conditions) gave poorer results, however, here again complete separation of Sr^{90} and Y^{90} was achieved (Fig. 4).

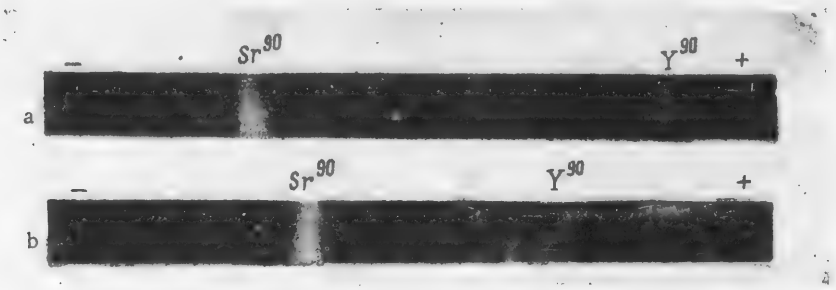

Fig. 4. Autoradiograph of the separation of Sr^{90} and Y^{90}: a) 0.1 M sodium ethylenediaminetetracetate; b) 0.03 M citric acid.

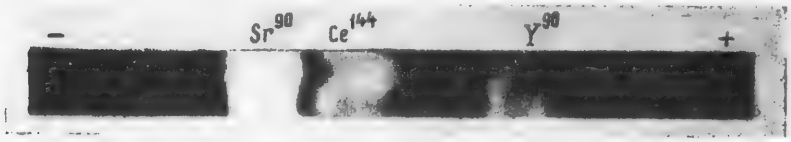

Fig. 5. Separation of Sr^{90}, Y^{90}, and Ce^{144}. Cathode solution – 0.03 M citric acid, pH 12; anode solution – 0.5 M HCl.

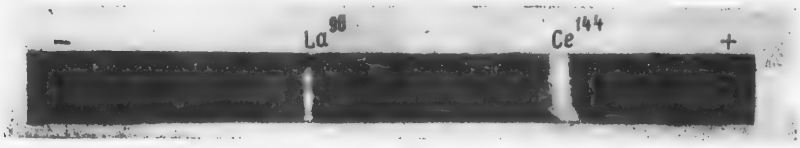

Fig. 6. Separation of La^{140} and Ce^{144} using a 0.5 M solution of sodium ethylenediaminetetracetate.

Separation of Sr^{90}, Y^{90}, and Ce^{144}. In the succeeding experiments, the possibility was established of separating Sr^{90}, Y^{90}, and Ce^{144} without introducing carriers. As in the previous series of experiments, citric acid and sodium ethylenediaminetetracetate were used.

The experimental conditions used, and the results obtained are given in Table 2.

The results given in Table 2 show that, as a rule, the distance between the zones for Ce^{144} and Y^{90} in citric acid are significantly greater than in sodium ethylenediaminetetracetate solutions.

TABLE 2

Cathode solution				Anode solution	Distance between the zones, mm	
Complexing agent	Concentration complexing agent, M	NaOH concentration, M	pH	HCl concentration, M	Sr and Ce	Ce and Y
Citric acid	0,01	***	12	0,5	30	45
" "	0,03	—	12	0,5	15	27
" "	0,05	—	12	0,5	8	20
" "	0,1	—	12	0,5	6	10
" "	0,5	—	12	0,5	0	4
" "	0,1*	0	—	0,5	—	—
" "	0,1	0,1	—	0,5	15	25
" "	0,1	0,3	—	0,5	10	20
" "	0,1	0,5	—	0,5	10	15
" "	0,1	0,8	—	0,5	6	10
" "	0,1**	1,0	—	0,5	0	0
" "	0,1	***	12	0,1	8	30
" "	0,1	—	12	0,3	8	16
" "	0,1	—	12	0,5	6	10
Sodium ethylenediaminetetracetate	0,1	***	9	0,03	12	4
" "	0,04	—	9	0,03	15	4
" "	0,02	—	9	0,03	30	6

*Not focused.

**Not separated.

***NaOH concentration constant.

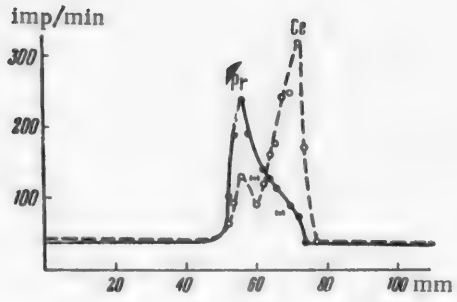

Fig. 7. Separation of Ce and P. Cathode solution — 0.025 M sodium ethylenediaminetetracetate, 0.025 M citric acid, pH 8; anode solution — 0.1 M HCl.

In Fig. 5 is shown an autoradiograph of a paper sheet on which Sr^{90}, Y^{90}, and Ce^{144} have been separated in citric acid.

Separation of La^{140} and Ce^{144}. Separation of La^{140} and trivalent Ce^{144}, taken without a carrier, was carried out as before by means of sodium ethylenediaminetetracetate and citric acid.

The effect of changing the concentration of sodium ethylenediaminetetracetate from 0.01 to 0.1 M in the cathode solution was studied. It was found that separation of La^{140} and Ce^{144} occurred only when the sodium ethylenediaminetetracetate concentration was 0.5 M. As can be seen from the autoradiograph (Fig. 6), the distance between the zones in this case was 35 mm.

Separation of Ce and Pr. Separation of a mixture of cerium (III) and praseodymium in concentrations up to 0.5 mg/ml was studied in another series of tests. Ce^{144} and Pr^{144} (T = 17.5 minutes) were used as radioactive indicators.

Complete separation of Ce and Pr was not achieved on using sodium ethylenediaminetetracetate. A mixture of sodium ethylenediaminetetracetate and citric acid (Fig. 7) gives the best results.

SUMMARY

A study has been made of the possibility of separating Sr^{90}–Y^{90}, Sr^{90}–Y^{90}–Ce^{144}, and Ce^{144}–La^{140}, all taken without carriers, as well as the possibility of separating a mixture of Ce–Pr, by the method of focusing ion exchange. It has been established that mixtures of Sr^{90}–Y^{90}, Sr^{90}–Y^{90}–Ce^{144}, and Ce^{144}–La^{140} can be separated in the course of five minutes when citric acid or sodium ethylenediaminetetracetate are used; separation of a mixture of Ce–Pr in concentrations up to 0.5 mg/ml is not complete.

LITERATURE CITED

[1] T.R. Sato, H. Diamond, and W.P. Norris, J. Am. Chem. Soc. 74, 6154-6155 (1952).

[2] T.R. Sato, W.P. Norris, and H.H. Strain, Analyt. Chem. 26, 267 (1954).

[3] T.R. Sato, W.P. Norris, and H.H. Strain, Analyt. Chem. 27, 521 (1955).

[4] P.N. Zimakov, A.G. Bykov, and M.A. Usachev, Report Read at the All-Union Conference on the Use of Radioactive and Stable Isotopes and Radiation in the Social Economy and in Science. Moscow, April 4-12, 1957.

[5] A. Kolin, Proc. Nat. Acad. Sci. USA 41, 101 (1955).

[6] H. Hoch and G.H. Barr, Science 122, 243 (1955).

[7] E. Schumacher, Helv. Chim. Acta 40, 1, 221 (1957).

[8] E. Schumacher and H.J. Streiff, Helv. Chim. Acta 40, 1, 228 (1957).

[9] E. Schumacher, Helv. Chim. Acta 40, 7, 2322 (1957).

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HYDRON II – A NEW INDICATOR FOR THE COMPLEXONOMETRIC DETERMINATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM

I.S. Mustafin and E.S. Kruchkova

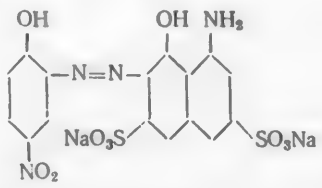
A number of indicators have been fairly successfully used for the complexonometric determination of total calcium and magnesium; they include: eriochrome black [1], acid chrome dark-blue, and acid chrome-blue K [2]; relatively recently some new, interesting indicator materials have been described [3, 4]. When one talks about the determination of one of the elements mentioned in the presence of the other, it should be borne in mind that an indicator cannot be found which will permit determination of magnesium in the presence of calcium, since sodium ethylenediaminetetracetate forms a less stable compound with magnesium than with calcium; the pH's of these complexes are, respectively, 8.69 and 10.59 [5].

Murexide is widely used as a complexonometric indicator for calcium in the presence of magnesium [6]; in the presence of magnesium, the change in the color of the solution being titrated from rose to lilac-violet at the end point is not sufficiently clear. Welcher [7] correctly notes that such an indicator change is far from complete.

New indicators have now been found which will permit complexonometric determination of calcium in the presence of magnesium. Calcion IREA [8], in particular, is such an indicator. This indicator gives a more contrasting color change at the end-point (from bright rose to blue) than murexide. The essential drawback of this indicator, however, is the high salt error, and the impossibility of determining calcium in the presence of appreciable amounts of magnesium.

Lake red [9] exhibits a very small contrast in color change, and is not characterized by high sensitivity (5-10 μg/ml Ca^{2+}). It has been established that it is possible to use acid chrome dark-blue and acid chrome-blue as indicators for the complexonometric titration of calcium in the presence of magnesium in an alkaline medium [10]. The indicator change is characterized by a change in color from red to lilac-blue. Diehl and Ellingbone [11] recommend calcein, which is a condensation product of iminodiacetic acid with fluorescein; the indicator change is not characterized by a contrasting change in color (from yellow-green to brown). Worthy of attention as indicators are the azo compounds: 1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulfonic acid [12] and 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid [13]. When calcium is titrated with a solution of sodium ethylenediaminetetracetate using these indicators there is a color change from red to blue. Unfortunately, we did not have these indicators at our disposal.

During a systematic study of the analytical possibilities of hydroxyazo compounds, we found materials which, in alkaline media, interact with calcium and are indifferent to magnesium. Of these, the most interesting compound proved to be the dye, acid chrome dark-green Zh:

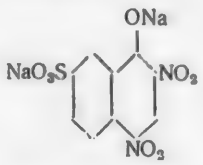


This material is a dark-brown powder which is readily soluble in water, but less soluble in alcohol; it is insoluble

in benzene, chloroform, and dioxane. An alkaline solution of the dye (pH 12.5) has a violet-blue color; in the presence of calcium ions a bright-red color develops. The reaction sensitivity is 0.5 μg/ml Ca^{2+}. Under these conditions, the dye does not interact with magnesium, but its solution acquires a deeper blue shade.

When this dye is used as an indicator, the bright-rose color of the solution being titrated (excess Ca^{2+}) changes to violet-blue (excess sodium ethylenediaminetetracetate). Of course, such a change does not possess sufficient contrast; accordingly, we decided to mix the indicator material with a suitable inert dye. The latter, being an internal light filter, should be capable of enhancing the contrast in the color change of the indicator. Some authors [14-16] have tried in this way to increase the contrast in the color change of murexide. The same approach was also tried by Kuznetsov [9] for improving the indicator change of lake red.

For a number of reasons we chose, as the inert dye, naphthol yellow:



aqueous solutions of which have a yellow color, the color being independent of the pH.

We have designated the mixed indicator consisting of acid chrome dark-green Zh and the internal light filter – naphthol yellow – "Hydron II." On titrating calcium with a solution of sodium ethylenediaminetetracetate in an alkaline medium (2 ml of 1 N NaOH to 50 ml of solution being titrated), using Hydron II as indicator, the color changes from bright rose to green. Hydron II exhibits a slightly higher sensitivity toward calcium than the original dye (0.1 μg/ml Ca^{2+}) as a result of the increase in contrast of the final colors.

We have studied the possibility of the complexonometric determination of calcium in the presence of various amounts of magnesium. Titration was carried out with 0.02 N sodium ethylenediaminetetracetate in the presence of 2 ml of 1 N NaOH per 50 ml of solution until there was a change from a rose color to green; usually during the titration a precipitate of magnesium hydroxide separates out.

TABLE 1

Titration of Calcium in the Presence of Magnesium

Ca^{2+} taken, mg	Molar ratio of Ca : Mg	Ca^{2+} found, mg
3.246	1 : 0	3.246
3.246	1 : 0.1	3.253
3.246	1 : 1	3.253
3.246	1 : 10	3.258
0.324	1 : 100	0.327

The results given in Table 1 indicate that Hydron II permits fully satisfactory results to be obtained for the determination of calcium in the presence of 100 times its amount of magnesium.

In an alkaline medium magnesium does not interact at all with the indicator. However, when large amounts of magnesium are present in the solution being titrated, copious precipitation of magnesium hydroxide occurs, and the adsorption processes which accompany this precipitation complicate establishment of the end point; in such cases, it is necessary to dilute the solution more.

Titration should be carried out immediately after addition of the alkali, otherwise, on standing, the adsorption processes which occur on the surface of the magnesium hydroxide intensify and the indicator change deteriorates. Careful agitation of the solution during titration leads to an increase in the sharpness of the color change at the equivalence point.

Ni^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, and Mn^{2+} interfere with calcium determination when Hydron II is used as indicator. Iron does not interfere at concentrations less than 1 mg/liter. When iron is present in larger amounts it depresses the results. When more than 200 mg/liter of iron is present titration of calcium becomes impossible because of the copious deposition of the brown hydroxide.

The presence of 20 mg of Al^{3+} per liter of test solution does not affect the titration results of any amount of calcium; when larger amounts of aluminum are present, the results obtained are somewhat low.

Hydron II has an insignificant salt error and permits titration of calcium in 10% NaCl solution, although, under such conditions, the contrast in the color change diminishes somewhat.

TABLE 2

Determination of the Calcium Hardness of Water Using Hydron II as Indicator

Test water	Hardness, mg·equiv/liter
Tap water	2.2302
Tap water diluted 10 times	0.2212
Tap water diluted 100 times	0.0228
Tap water diluted 500 times	0.0054

The results given in Table 2 indicate that Hydron II permits satisfactory determination of the calcium hardness of water with a low mineral content (5 μg-equiv/liter).

In order to determine the calcium hardness, 2 ml of 1 N NaOH is added to 50 ml of test water, followed by four to five drops of Hydron II (excess indicator impairs the color change). A bright-rose color develops. Titration is carried out with careful stirring of the solution. The concentration of the sodium ethylenediaminetetracetate solution is varied within the limits 0.02-0.002 N, depending on the mineral content of the water. For the determination of the hardness of water with a very low mineral content by means of 0.002 N sodium ethylenediaminetetracetate, the titration is carried out using a control, in which calcium has been titrated beforehand in an alkali solution, since Hydron II is sensitive to calcium ions contained in it (to 50 ml of distilled water is added 2 ml of 1 N NaOH and this is titrated in the presence of Hydron II).

Hydron II is prepared by mixing one volume of a 0.5% aqueous solution of acid chrome dark green Zh and two volumes of a 0.25% aqueous solution of naphthol yellow.

Both these materials are produced by Russian industry and are used in dye work. The indicator solution does not deteriorate on storage.

SUMMARY

A new indicator containing an internal light filter is proposed for the complexonometric determination of calcium in the presence of magnesium; it is called "Hydron II." The indicator permits determination of calcium in the presence of 100 times its amount of magnesium.

It has been shown that it is possible to determine the calcium hardness of water of low mineral content (5 μg-equiv/liter) using Hydron II as indicator.

LITERATURE CITED

[1] G. Schwarzenbach and W. Biedermann, Helv. Chim. Acta 31, 678-87 (1948).

[2] T.V. Styunkel', E.M. Yakimets, and D.A. Savinovskii, Zhur. Anal. Khim. 8, 163 (1953).*

[3] I.S. Mustafin and E.A. Kashkovskaya, Zavodskaya Lab. 23, 519 (1957).

[4] I.S. Mustafin, E.A. Kashkovskaya, and A.N. Ivanova, Zavodskaya Lab. 24, 1060 (1958).**

[5] R. Prshibil, Complexones in Chemical Analysis [Russian translation] (IL, Moscow, 1955) p. 29.

[6] G. Schwarzenbach and H. Gysling, Helv. Chim. Acta 32, 1314 (1949).

*Original Russian pagination. See C.B. translation.

**See English translation.

[7] F. Welcher, The Analytical Uses of Ethylenediamine Tetraacetic Acid (New York, 1957) p. 61.

[8] The All-Union Scientific Research Institute of Chemical Reagents: "Basic Instructions on the Analytical Use of a New Reagent for Calcium-Calcion IREA."

[9] V.I. Kuznetsov and V.A. Mikhailov, Zhur. Anal. Khim. 12, 59 (1957).*

[10] T.B. Styunkel' and E.M. Yakimets, Zavodskaya Lab. 24, 23 (1958).**

[11] H. Diehl and J. Ellingboe, Analyt. Chem. 28 (1958).

[12] H. Hilderbrand and Ch. Reilley, Analyt. Chem. 29, 258 (1957).

[13] J. Patton and W. Reeder, Analyt. Chem. 28, 1026 (1956).

[14] A. Knight, cited in Chemical Abstracts 48, 915 (1954).

[15] R. Routil, cited in Referat. Zhur. Khim. 10974 (1958).

[16] J. Piglowski, cited in Referat. Zhur. Khim. 24748 (1958).

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**See English translation.

SPECTROGRAPHIC DETERMINATION OF ALUMINUM IN URANIUM

E.A. Vernyi and V.N. Egorov

The difficulties which are encountered during the spectrographic determination of aluminum in uranium are determined, in the main, by the rather low volatility of aluminum oxide, and the very intense and multilinear spectrum of uranium. In view of the latter circumstance, all those methods which are based on the complete burning of the sample in the spectrum excitation source cannot ensure a sufficiently sensitive determination of aluminum. Unsatisfactory results are obtained even when aluminum is determined in uranium by the evaporation method [1-3]. Because of the small difference in the vapor pressure of aluminum oxide and uranoso-uranic oxide, the aluminum does not evaporate completely and this depresses the experimental accuracy considerably. The conditions for evaporating the aluminum improve somewhat on adding carbon powder. However, even in this case, the experimental accuracy is not high. When the sensitivity of the determination of aluminum is $1 \cdot 10^{-3}$%, the reproducibility amounts to 20-30%. Moreover, the given method of determining aluminum, like all other methods based on separating impurities from the main element with their subsequent excitation, is fairly difficult.

Worthy of particular attention for the determination of aluminum in uranoso-uranic oxide is the method of fractional distillation with a carrier, which was used for the first time for uranium by Scribner and Mullin [4]. This method makes it possible to create in the excitation source of the spectrum conditions which will ensure, in the main, that only the impurities are evaporated and excited, so that the spectrum of the base element is thereby weakened appreciably while the spectrum of the impurities is strengthened. In order to excite the spectrum, Scribner and Mullin use a dc arc fed with a current of 10 amp. They used gallium oxide added in amounts of 2% to the test sample as a carrier. The electrode consisted of a graphite basin of a special shape and a carbon support which ensured only a small amount of heat leakage from the sample. The amount of sample taken was 100 mg. The determination was carried out on the basis of the lines Al 3082.16 and 3092.71. The sensitivity of the method amounts to 0.5 γ or $5 \cdot 10^{-4}$% Al.

We have developed a comparatively simple method for determining aluminum in uranium ($1\ 10^{-3}$ to $3 \cdot 10^{-2}$% Al) using fractional distillation and a carrier.

The success of the method depends to a significant extent on the electrode design. The electrode that proved to be most suitable is the one shown in Fig. 1. Such electrodes ensure rapid and uniform heating of a sample with a very small mechanical increase in the amount of the material in the discharge zone. In choosing a carrier it was desirable to use the same material both as carrier and internal standard. Of the materials tested (AgCl, $SrCO_3$, and $BaCO_3$), barium carbonate proved to be the most suitable. Experiments were carried out to establish the effect of barium carbonate and carbon powder on the intensity of the aluminum lines. The significant effect manifested by carbon powder on the evaporation of aluminum from uranoso-uranic oxide, obviously is the result of a partial reduction of aluminum oxide, with subsequent rapid passing of the aluminum atoms into the discharge zone, as a result of which the aluminum lines increase significantly in strength and the uranium spectrum is weakened. Carbon powder is effective at concentrations of 3% and over. Barium carbonate leads to the same results; however, its mode of action is different. Barium, obviously, while not essentially affecting the evaporation of aluminum from the sample, creates favorable conditions for the excitation of aluminum. This assumption, which is used to explain the role of carrier at present [5, 6] was verified experimentally by us. The experiments which were carried out to check the effect of barium on the line intensity of aluminum, were similar to those which were carried out previously [5]. The electrode used for this purpose is shown in Fig. 2. In one case, a mixture of uranoso-uranic oxide and barium carbonate was placed in the circular crater of the electrode; in another case, the same amounts of uranoso-uranic oxide and barium carbonate were placed separately in the

crater. Within the limits of experimental error, the blackening of the aluminum lines proved to be the same in both cases. In addition, the "burning out" of aluminum and barium was studied by photographing the spectra on a moving film. As one might have expected, the aluminum "burnt out" somewhat slower than barium, while the picture was identical in both cases. It should be noted that aluminum is only efficiently excited in the presence of a sufficient amount of barium atoms in the discharge plasma. The aluminum lines weaken on the spectrogram

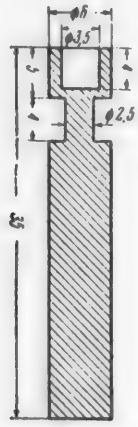

Fig. 1.

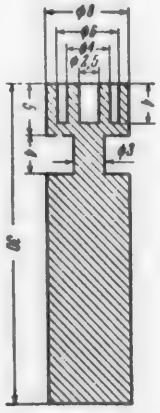
Fig. 2.

at the same time as the barium lines, and then disappear. Addition of a new lot of barium to the same electrode containing the test sample leads to an increase in the intensity of the aluminum lines. An identical experiment carried out with uranoso-uranic oxide mixed with barium carbonate and 5% of carbon powder, showed that in the presence of carbon powder both aluminum and barium evaporate almost completely from the sample in 20-30 seconds. In this case, addition of a new lot of barium did not lead to the appearance of the aluminum lines.

From what has been said, it is clear that barium essentially affects the evaporation of aluminum from uranoso-uranic oxide, and significantly improves the excitation conditions of the aluminum atoms.

TABLE 1

Comparison of the Results of Spectrographic and Chemical Methods of Determining Aluminum

Sample	Method		Sample	Method	
	chemical	spectro-graphic		chemical	spectro-graphic
1	$5 \cdot 10^{-3}$	$6 \cdot 10^{-3}$	4	$3.8 \cdot 10^{-2}$	$3.3 \cdot 10^{-2}$
2	$1.1 \cdot 10^{-2}$	$1.3 \cdot 10^{-2}$	5	$2.3 \cdot 10^{-2}$	$2.2 \cdot 10^{-2}$
3	$4 \cdot 10^{-3}$	$4.5 \cdot 10^{-3}$	6*	$9 \cdot 10^{-3}$	$1 \cdot 10^{-2}$

*The sample contained 1.3% Mo.

On the basis of the results of these experiments, we chose the following conditions for determining aluminum. Barium carbonate and carbon powder were added to the samples of uranoso-uranic oxide in amounts of 10 and 5%, respectively (100 mg $BaCO_3$ and 50 mg of carbon powder to 1 g of U_3O_8). 25 mg aliquots of test material and standards were placed in the specially designed electrode (Fig. 1). The spectra were excited in an ac arc at a current strength of 18 amp. The upper electrode was a carbon rod sharpened to a truncated cone with an area of 2 mm. Exposure time was 30 seconds. The spectra were photographed on a ISP-51 spectrograph with a UF-85 camera. The slit was illuminated with a one-lens condenser. The slit width was 10-15 μ. The analytical lines Al 3944.03 and Ba 3995.66 are not overlapped by uranium lines.

Calibration curves constructed within the coordinates (ΔS, log C) were linear within the concentrations

$1 \cdot 10^{-3}$ to $3 \cdot 10^{-2}$%. The sensitivity of the determination of aluminum under the conditions chosen is 0.25 γ or $1 \cdot 10^{-3}$% Al, and, when necessary, can be increased. Evaluation of the reproducibility of the method was carried out on samples with aluminum contents of $5 \cdot 10^{-3}$, $1.3 \cdot 10^{-2}$, and $2.2 \cdot 10^{-2}$%. The relative mean-square error of a determination on taking three parallel spectrograms for a sample was 9-11% for this concentration range.

Results of the determination of aluminum by the spectrographic method and by a chemical method are given in Table 1.

TABLE 2

Effect of Third Elements on the Results of Aluminum Determination*

Element	Not introduced	Impurities introduced, %							
		0,1	0,3	1,0	1,3	3	5	7	10
Na (form of Na_2CO_3)	$9 \cdot 10^{-3}$	$8,3\ 10^{-3}$	$8,5 \cdot 10^{-3}$	$9,1 \cdot 10^{-3}$	—	$9,5 \cdot 10^{-3}$	—	—	—
CaF_2	$9 \cdot 10^{-3}$	$9,7 \cdot 10^{-3}$	$8,6 \cdot 10^{-3}$	$9,2 \cdot 10^{-3}$	—	$9,8 \cdot 10^{-3}$	—	—	—
Fe (form of Fe_2O_3)	$9 \cdot 10^{-3}$	$8,7 \cdot 10^{-3}$	$9 \cdot 10^{-3}$	$6,5 \cdot 10^{-3}$	—	—	—	—	—
Mo (form of MoO_3)	$9 \cdot 10^{-3}$	—	—	—	$9,1 \cdot 10^{-3}$	$8,8 \cdot 10^{-3}$	$8,3 \cdot 10^{-3}$	$8,2 \cdot 10^{-3}$	$6,4 \cdot 10^{-3}$

*Mean of 4-5 plates.

The method described, in contrast to the evaporation method, can be used for samples containing large amounts of impurities. The presence of large amounts of barium (7%), which, in the main, determines the excitation conditions of the impurities in the discharge, significantly weakens the effect of third elements. It is clear from Table 2 that no appreciable effect on the results of aluminum determination is shown by CaF_2 (for amounts up to 3%), Fe (up to 0.3%), Na (up to 3%), and Mo (up to 5-7%).

SUMMARY

A spectrographic method which has been developed for the determination of small amounts of aluminum in uranium is based on the phenomenon of fractional distillation with a carrier. Some experiments have been carried out with the aim of studying the effect of barium and carbon powder on the intensity of aluminum lines. The effect of third elements on the results of aluminum determination has been studied.

LITERATURE CITED

[1] A.N. Zaidel', N.I. Kaliteevskii, L.V. Lipis, M.P. Chaika, and Yu.I. Belyaev, Zhur. Anal. Khim. 11, 21 (1956).*

[2] S.L. Mandel'shtam, N.N. Semenov, and Z.M. Turovtseva, Zhur. Anal. Khim. 11, 9 (1956).*

[3] L.V. Lipis, Zavodskaya Lab. 24, 736 (1958).**

[4] B.F. Scribner and H.R. Mullin, J. Res. Nat. Bur. Stand. 37, 379 (1946).

[5] A.N. Zaidel', N.I. Kaliteevskii, G.G. Kund, and Z.G. Fratkin, Optika i Spektroskopiya 2, 28 (1957).

[6] E.E. Vainshtein and Yu.I. Belyaev, Zhur. Anal. Khim. 13, 388 (1958).*

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*Original Russian pagination. See C.B. translation.

**See English translation.

SPECTROGRAPHIC DETERMINATION OF SCANDIUM IN ORES

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Information on the distribution of scandium in nature is mainly based on the results of semiquantitative spectrographic analysis [1]. Known methods for the quantitative spectrographic determination of scandium relate either to the analysis of minerals containing scandium, or to the analysis of monotypic ores, and require in each separate instance the use of appropriate standards similar in composition to the test samples [2-6]. A determination of scandium in which this element was removed beforehand with calcium or thorium, and in which the effect of the composition of the test sample on the analytical results was eliminated, has been described by Solodovik, Rusanov, and Kondrashina [5]. It should be pointed out, however, that preliminary chemical treatment of ores and minerals in order to level the composition of the test samples, and in order to increase the scandium concentration, lengthen the determination considerably, and, in some cases, leaves one in doubt as to whether all the scandium has been separated. Accordingly, methods for the direct determination of scandium in ores are of undoubted interest.

The present article contains a description of a method for the direct determination of thousandths of a percent of scandium in silicate ores, the results obtained being dependent on the composition of the test silicates to a comparatively small extent.

The test ore, diluted with buffer powder consisting of carbon and strontium carbonate, is evaporated in an horizontal ac arc [7] which has been used previously for the quantitative determination of beryllium in ores [10]. Such a position of the electrode ensures uniform passage of the elements into the arc flame, the latter occupying a stable position with respect to the electrodes. The evaporation products are continuously removed by the ascending stream of air from the discharge zone, and do not condense on the upper electrode, as happens when the electrodes are fixed vertically. A characteristic feature of a horizontal arc is the constancy of the distribution of the excitation conditions in the arc cloud during the uniform evaporation of the elements with low ionization potentials which compose the buffer powder.

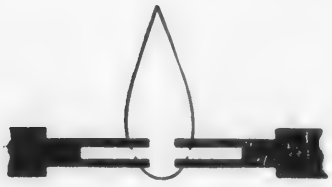

Fig. 1. Graphite electrodes and the image of the arc flame.

During evaporation of silicate ores and products obtained during their technological processing, ash, coal, etc., scandium passes into the arc flame almost at the same time as strontium and those elements located toward the end of the volatility series of the oxides in a carbon arc (rare earths, thorium, niobium, tantalum, zirconium, etc.). The arc is ignited by bringing together the electrode tips and does not require the use of high-frequency currents. After the mixtures of buffer powder and test ore have evaporated, the burning of the arc ceases of itself.

Scandium is determined on the basis of its most sensitive line 4246.83 A, which appears when only ten thousandths of a percent of scandium is present in the test ores. Lanthanum, which is most frequently used for the determination of scandium [3], is used as the standard; lanthanum is added in small amounts in the form of its oxide to the buffer mixture.

The scandium content of the ores is found from the curve relating the logarithm of the relative intensity of the scandium and lanthanum lines to the logarithm of the percentage content of scandium in standards.

The relative intensity of the scandium and lanthanum lines is evaluated by photometric interpolation [8]. This method, which depends to only a small extent on the properties of the photographic plate emulsion, made it possible to obtain a linear calibration curve in the regions of low blackening. The standards used arc powders made by mixing pure scandium oxide with a powder consisting of two parts of quartz and one part of feldspar. Scandium is determined quantitatively in a concentration range from thousandths to hundredths of a percent, with a mean probable error of ±10% when the spectrum of a sample is photographed once.

TABLE 1

Analytical Lines

Analytical lines	Excitation potential of the lines, ev	Concentration range over which scandium is determined, %	Composition of buffer mixture	Dilution of ore by buffer mixture	Interfering elements and control line, A	Error of a single determination, %
Sc II 4246,83, La II 4263,58	3,23 4,86	0,001—0,1	Carbon powder and $SrCO_3$ 1:1	1 : 3	Ce 1% Ce 4246,4 Ce 4248,6	±10% ±10%
Sc II 4246,83, La II 4269,49	3,23 4,69	0,001—0,1	Ditto	1 : 3	Ce 4248,6	

The analytical lines are given in Table 1.

0.05 g of test ore is mixed with 0.15 g of buffer mixture consisting of equal parts by weight of carbon and strontium carbonate; 0.5% of lanthanum oxide is added to the buffer mixture.

The mixture of powders is carefully ground in an agate mortar in the presence of alcohol. The mixture of powders is evaporated completely from the opening in two carbon electrodes (Fig. 1), the diameter of this opening being 2 mm and its depth 8 mm.

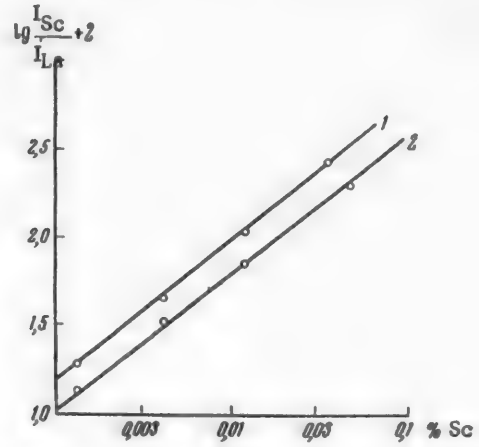

Fig. 2. The relation between the relative intensity of the scandium and lanthanum lines and the scandium concentration of the ore: 1) Sc II – 4246.83 and La II – 4263.58; 2) Sc II – 4246.83 and La II – 4269.49.

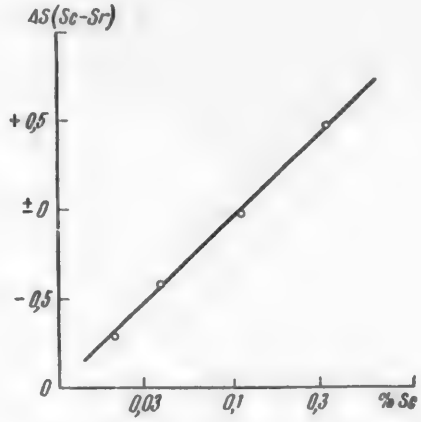

Fig. 3. The relation between the difference in blackening of the lines Sc 2552.36 and Sr 2423.6, and the scandium content of the ore.

The electrodes are fitted up in a horizontal position and an ac arc struck between them (15 amp, 220 volt). The arc gap, which is 4 mm, is kept constant during arc burning. The light from the central part of the arc flame is directed by means of a three-lens illuminating system onto the slit of an autocollimating KS-55 spectrograph fitted with glass optics. The opening in the intermediate diaphragm of the illuminating system is 2 mm.

The spectra are photographed through a ten-stage attenuator fitted in front of the spectrograph slit, on diapositive plates with a sensitivity of 0.8 GOST units. The spectrograms are examined under a spectroprojector, and the equation for the degree of blackening [9] of scandium and lanthanum lines found for each test sample.

Using calculating tables, the blackening is converted to the logarithm of the relative intensity of the analytical pairs of lines:

Sc II 4246.83 and La II 4263.58;

Sc II 4246.83 and La II 4269.49.

In Fig. 2 is shown the calibration curve relating the logarithm of the relative intensity of the pairs of lines to the scandium content of standards.

The experimental results for the scandium content of ores as found by the method described depend only to a small extent on the composition of the ores, and permit analysis of various silicate ores using one series of standards prepared from quartz and feldspar. To illustrate this, there are given in Table 2 analytical results obtained for mineral powders with widely varying contents of silicon, calcium, magnesium, iron, aluminum, and the alkaline metals (feldspar), which usually enter into the composition of silicates.

Changes in the composition of the test material do not affect the results for scandium (Table 2). It should be pointed out that cerium, when present in the ore in amounts upward of 1%, interferes with scandium determination, since the weak line of Ce 4246.4 which is present in the cerium spectrum overlaps the analytical line of scandium.

TABLE 2

Composition of test sample	Scandium		Relative error of a single determination
	taken, %	found, %	
Quartz	0,0185	0,0180	—2,7
Quartz 50% and feldspar 50%	0,0185	0,0180	—2,7
"	0,041	0,042	+2,4
Quartz 50% and Al_2O_3 50%	0,041	0,040	—2,4
Quartz 50% and $CaCO_3$ 50%	0,0060	0,0060	±0
"	0,041	0,045	+9,8
Quartz 50% and MgO 50%	0,0185	0,0190	+2,7
D "	0,041	0,044	+7,3
Quartz 50% and Fe_2O_3 50%	0,0185	0,0190	+2,7
"	0,041	0,036	—12,2

The control line for cerium, the appearance of which indicates the possibility of errors arising as a result of the presence of the overlapping line in the spectrum, is the line Ce 4246.4.

The test ore should not contain more than 0.1% of lanthanum either, since the latter is used as the internal standard and is added in a constant amount to the ore.

When cerium and lanthanum are present, scandium can be determined on the basis of its lines in the ultraviolet; this line is obtained by means of the ISP-22 quartz spectrograph or by the autocollimating KS-55 spectrograph with quartz optics; determinations are based on measurements of the difference in blackening of the lines Sc 2552.36 and Sr 2423.6. The concentration range for which scandium can be determined by the pair of lines indicated is 0.02-0.4%. Iron (in amounts greater than 20%) and thorium (greater than 1%) interfere when scandium is determined by this technique. The appearance of the control line Fe 2553.2 in the spectrum of the ore indicates the danger of overlapping of the Sc 2552.36 by the interfering iron line, while the appearance of the control line Th 2404.17 indicates the danger of the line Sr 2423.6 being overlapped by one of the lines in the thorium spectrum.

The calibration curve relating the difference in blackening of the lines Sc 2552.36 and Sr 2423.6 to the percentage scandium content of the ore is shown in Fig. 3.

SUMMARY

By using as spectrum excitation source a horizontal ac carbon arc stabilized with strontium carbonate, it is possible to determine scandium directly in the concentration range 0.001 to 0.1% in silicate ores of varying composition; the probable error for a single determination is ±10%.

LITERATURE CITED

[1] V.M. Goldschmidt, Cl. Peters, Ges. Wiss. Göttingen, Math.-Physik 1, 257 (1931).

[2] L.H. Ahrens, Spectrochem. Analysis (Cambridge, 1950).

[3] A. Kvalheim and W. Strock, Spectrochem. Acta 1, 221 (1939).

[4] S.A. Borovik, Doklady Akad. Nauk SSSR 36, 186 (1942).

[5] S.M. Solodovik, A.K. Rusanov, and A.I. Kondrashina, Zhur. Anal. Khim. 12, 372 (1957).*

[6] O.A. Kul'skaya and O.F. Vdovenko, "Transactions of the Seventh Conference on the Analysis of the Ores of Rare and Scattered Elements." Ministry of Geology and Mineral Resources (in the press).

[7] A.K. Rusanov and V.M. Alekseeva, Zhur. Anal. Khim. 9, 183 (1954).*

[8] L.E. Vvedenskii, Quantitative Spectrographic Analysis of Magnesium Alloys Based on Aluminum, Zinc, Manganese, and Beryllium [in Russian] (Oborongiz, Moscow, 1940).

[9] V.K. Prokof'ev, Photographic Methods of Quantitative Spectrographic Analysis of Metals and Alloys [in Russian] (Gosteoretizdat, Moscow-Leningrad, 1951) p. 80.

[10] V.M. Alekseeva and A.K. Rusanov, Zhur. Anal. Khim. 12, 23 (1957).*

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QUANTITATIVE DETERMINATION OF SCANDIUM BY MEANS OF MANDELIC ACID

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The analytical chemistry of scandium has not hitherto been developed sufficiently [1]. Inorganic precipitants such as hydrogen fluoride, silicofluoric acid, pyrophosphoric acid [2], and hypophosphoric acid [3], etc., have been recommended for the quantitative determination of scandium and for its separation from other elements. Organic precipitants have been studied to a considerably lesser extent; mention could be made of oxalic acid, 8-hydroxyquinoline [4] and its halogen derivatives [5], and sodium alizarinsulfonate [6]. Phytic acid [7] has proved to be the most selective precipitant. Scandium can also be precipitated by phenylarsonic acid. A number of color reactions are also known for scandium, the most interesting of these is the color reaction with azo compounds containing the arsono group [8]. Recently, extraction with organic solvents [9] has been successfully used for separating scandium; ion-exchange chromatography has also been successfully used [10].

Examination of the chemicoanalytical reactions of the scandium ion reveals that it has many properties in common with thorium ions, and, particularly, with zirconium and hafnium ions; the radii of the ions of the last two elements are very similar to the radius of the scandium ion. In addition, scandium ions, just like those of zirconium, tend to polymerize [11]. This fact opens up the possibility of carrying out a search for new reactions and reagents for scandium, using the analogy indicated, and to use differences in the values of the pH of the solution during reactions with organic reagents. Thus, scandium, like thorium and zirconium, can be precipitated by organic derivatives of selenious or tellurious acids [12].

Our experiments have shown that scandium is precipitated in a weakly acid medium by mandelic acid, which, as is known, is a fairly selective reagent for zirconium [13-18]. In the work described in the present article, a study was made of the conditions for precipitating scandium with mandelic acid, and of the composition of the precipitate formed, while a method is described for separating scandium from the rare earths and from thorium.

EXPERIMENTAL

Standard scandium solution. 0.5 g of spectrographically pure scandium oxide was dissolved in 20 ml of concentrated hydrochloric acid with continuous careful stirring until the turbidity disappeared; the solution was carefully evaporated almost to dryness, and the residue dissolved in 500 ml of water. The solution was standardized by precipitating the scandium as hydroxide and weighing it as Sc_2O_3.

Scandium was precipitated with mandelic acid as follows.

To 35 ml of the solution of scandium salt was added 15 ml of an 8% solution of mandelic acid. After heating on a water bath for 30 minutes, and then cooling to room temperature, the white, flocculent precipitate which separated out was filtered, washed with 0.5% mandelic acid solution, dried, and finally calcined at 800° to constant weight.

In order to establish the optimum conditions for precipitating scandium, the effect of the concentration of reagent, and of the pH of the solution was studied. For this purpose, various amounts of an 8% solution of mandelic acid were added to a solution containing scandium (0.00495 g Sc_2O_3), the precipitates formed were then treated as described above. The experimental results obtained are shown in Fig. 1.

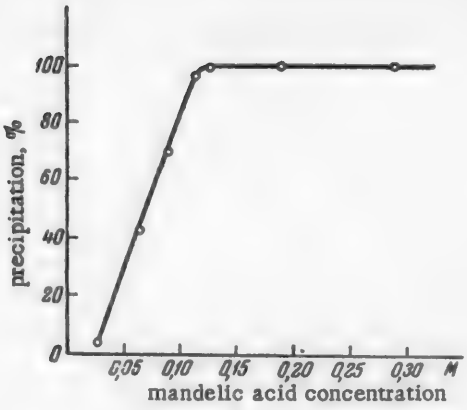


Fig. 1. Effect of mandelic acid concentration on completeness of scandium precipitation.

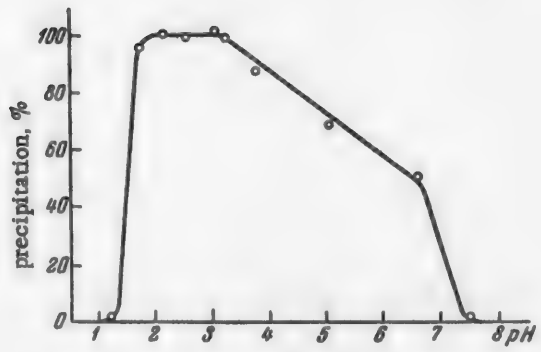
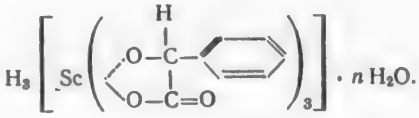


Fig. 2. Effect of pH on completeness of scandium precipitation.

In order to establish the relation between completeness of separation of scandium and the pH of the solution, precipitation with mandelic acid was carried out at various pH values, the pH's being adjusted by means of hydrochloric acid and ammonia. The pH of the filtrates was measured with a glass electrode. The results obtained are given in Fig. 2.

In order to achieve complete precipitation of scandium, it was found necessary to add excess of the reagent, and to maintain the pH of the solution in the range 1.8-3.2. It should be pointed out that zirconium, in contrast to scandium, is precipitated in a solution containing 5-7 N HCl. Results for the quantitative determination of scandium in a solution of its salt are given in Table 1.

Composition and properties of the compound. In order to study the composition of the compound formed between scandium and mandelic acid, the precipitate obtained was filtered through a glass crucible, and washed with a 0.5% mandelic acid solution; traces of mandelic acid were then removed by giving the precipitate a further washing with ether in which it is insoluble; the precipitate was finally dried at 110° and weighed. Part of the precipitate (about 20-50 mg) was calcined to constant weight at 800°, and the oxide Sc_2O_3 obtained, weighed. The results (Table 2) show that the composition of the precipitate isolated from a weakly acid medium (pH 2.5), corresponds to the formula $H_3[Sc(C_8H_6O_3)_3] \cdot nH_2O$. This compound, like zirconium mandelate [13, 19, 20], probably has the following structure:



The precipitates always contain coprecipitated mandelic acid as impurity; accordingly it should be removed by washing with ether before the precipitate obtained is weighed; however, more reliable results are obtained by weighing the scandium oxide obtained by calcining the precipitate.

The thermogram obtained on a continuous thermogravimetric balance (Fig. 3) shows that the compound is stable up to 280°; decomposition is observed at higher temperatures. In the range 340-390° an intermediate compound is formed which changes into scandium oxide at 500°.

The scandium precipitate, like the analogous compounds of zirconium [21] and hafnium [22] is readily soluble in ammonia. We studied the composition of this compound by Hahn's method [22], which was used for studying the similar complex compound of hafnium.

A known amount of the precipitate, obtained as described above, was dissolved in excess of a standard solution of ammonia 0.092 N, after which excess ammonia was titrated with 0.1 N hydrochloric acid using a glass electrode. The experimental results obtained are given in Table 3 and Fig. 4; they give a basis for assuming that dissolution of the precipitate in ammonia follows the following equation:

TABLE 1

Precipitation of Scandium with Mandelic Acid

Sc_2O_3, mg		Error		Sc_2O_3, mg		Error	
taken	found	mg	%	taken	found	mg	%
9,90	9,92	+0,02	20,2	4,95	4,90	−0,05	−1,0
9,90	9,90	±0,00	±0,0	4,95	4,98	+0,03	+0,6
4,95	4,95	±0,00	±0,0	0,99	1,02	+0,03	+2,0
4,95	4,94	−0,01	−0,2	0,99	0,98	−0,01	−1,0

TABLE 2

Analysis of the Compound Formed Between Scandium and Mandelic Acid

Weight of precipitate (mg)	Found, mg		Molar ratio, Sc
	Sc	$C_8H_7O_3$	$C_8H_7O_3$
24,5	2,2	22,3	1:3,0
34,1	3,0	31,1	1:3,1
55,7	4,9	50,8	1:3,1
55,1	4,9	50,2	1:3,0

TABLE 3

Determination of the Composition of the Precipitate after Dissolving it in Ammonia

Weight of precipitate, mg	Total volume of NH_4OH, ml	Volume of HCl solution, ml	Excess NH_4OH, ml	NH_4OH used for dissolving precipitate, ml	Ratio NH_4OH / $H_3[Sc(C_8H_6O_3)_3]$
71,6	25,0	18,4	20,2	4,8	3,1 : 1
105,5	25,0	16,6	18,2	6,8	3,0 : 1
150,4	25,0	13,6	14,9	10,1	3,1 : 1
175,0	25,0	12,5	13,7	11,3	3,0 : 1
226,2	25,0	9,5	10,4	14,6	2,9 : 1

TABLE 4

Determination of Scandium in the Presence of the Rare Earths

Ratio Sc: total rare earths	Sc_2O_3, mg		Error		No. of precipitations
	taken	found	mg	%	
1 : 1	2,97	3,12	+0,15	+5,0	1
	2,97	3,13	+0,16	+5,3	
	2,97	2,97	±0,00	±0,0	2
	2,97	3,01	+0,04	+1,3	
	2,97	2,95	−0,02	−0,7	
1 : 5	2,97	3,15	+0,18	+6,0	2
	2,97	3,10	+0,13	+4,3	
	2,97	3,04	+0,07	+2,3	3
	2,97	2,93	−0,04	−1,3	
1 : 10	2,97	2,96	−0,01	−0,3	3
	2,97	3,03	+0,06	+2,0	

TABLE 5

Determination of Scandium in the Presence of Thorium (Ratio Sc : Th = 1 : 1)

Sc_2O_3, mg		Error		No. of precipitations
taken	found	mg	%	
4,95	4,97	+0,02	+0,4	1
4,95	5,05	+0,10	+2,0	1
2,97	3,02	+0,05	+1,8	1
2,97	3,00	+0,03	+1,0	2

$$H_3[Sc(C_8H_6O_3)_3] + 3NH_4OH \rightleftarrows (NH_4)_3[Sc(C_8H_6O_3)_3] + 3H_2O.$$

The precipitate is also soluble in organic bases such as pyridine and ethylenediamine. Scandium hydroxide is formed by the action of sodium hydroxide. It is clear from the titration curve (Fig. 4) that the precipitate is soluble in ammonia at pH greater than 6.3.

Separation of scandium from the rare earths and thorium. At pH 2-3 the rare earths and thorium do not give a precipitate with mandelic acid; accordingly, it is possible to separate them from scandium. For this pur-

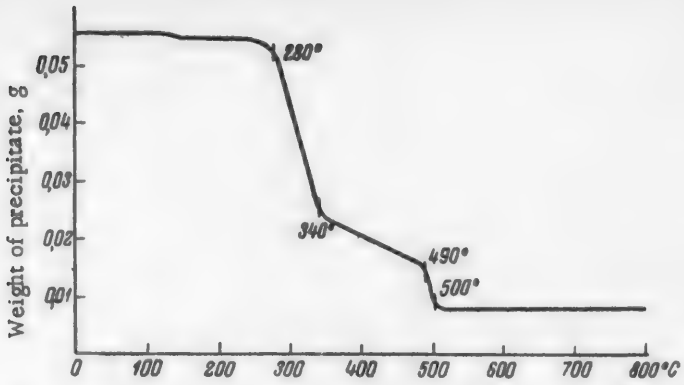


Fig. 3. Thermogravigram of the precipitate $H_3[Sc(C_8H_6O_3)_3] \cdot nH_2O$.

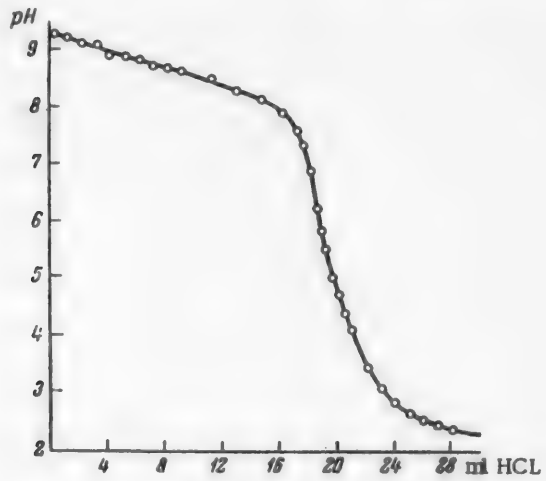


Fig. 4. Potentiometric titration of an ammoniacal solution of scandiomandelic acid with hydrochloric acid.

pose, standard solutions of the nitrates of the rare earths and thorium were taken. Precipitation was carried out as described above. It is necessary to carry out a reprecipitation in order to remove the rare earths quantitatively. For this purpose, the ready solubility of the precipitate in concentrated ammonia was used, the ammonia was added dropwise onto the filter. After washing the filter with distilled water, the solution was neutralized with 4 N HCl until it gave an acid reaction to methyl orange; 15 ml of 8% mandelic acid was added and the solution heated on a water bath for 30 minutes; after cooling, the precipitate was filtered through the same filter.

Results for the determination of scandium in the presence of the rare earths are given in Table 4.

Separation of scandium from thorium was carried out in the same way. It should be noted that large amounts of thorium interfere with scandium determination.

When the pH is increased, coprecipitation of thorium is observed. We tried to complex thorium by means of certain organic acids such as trihydroxyglutaric or lactic acid; however, it was found that scandium is also masked by these acids and does not give a precipitate. Results for the separation of scandium from thorium are given in Table 5.

SUMMARY

A new method has been developed for the quantitative determination of scandium by means of mandelic acid; a method has also been developed for separating scandium from the rare earths and thorium. The compo-

sition of the precipitate formed corresponds to the formula $H_3[Sc(C_8H_6O_3)_3] \cdot nH_2O$. The thermogravigram showed that the compound starts to decompose at 280°. Scandium mandelate dissolves in ammonia to form the compound $(NH_4)_3[Sc(C_8H_6O_3)_3]$.

LITERATURE CITED

[1] "Scandium," Collection of Translations edited by L.N. Komissarova [Russian translation] (IL, Moscow, 1958).

[2] G. Beck, Mikrochemie ver Mikrochim. acta 37, 790 (1951).

[3] D.K. Bomberger, Analyt. Chem. 30, 1907 (1958).

[4] L. Pokras and H.R. Bernays, Analyt. Chem. 23, 757 (1951).

[5] T. Moeller and M.V. Raman , J. Am. Chem. Soc. 76, 6030 (1954).

[6] G. Beck, Mikrochim. acta 2, 9 (1937).

[7] G. Beck, Mikrochemie ver. Mikrochim. acta 34, 62, 282 (1948).

[8] V.I. Kuznetsov, Zhur. Obshchei Khim. 14, 897 (1944).

[9] G.H. Morrison and H. Freiser, Solvent Extraction in Analytical Chemistry (New York, 1957).

[10] E. Lederer and M. Lederer, Chromatography (Amsterdam, 1953).

[11] L. Pokras, J. Chem. Educ. 33, 16, 284 (1956).

[12] I.P. Alimarin and V.S. Sotnikov, Vestnik Moskva Univ. 6, 137 (1957).

[13] C.A. Kumins, Analyt. Chem. 19, 376 (1947).

[14] A.A. Astanina and E.A. Ostroumov, Zhur. Anal. Khim. 6, 27 (1951).

[15] M. Venkataraman and Bh.S.V.R. Rao, J. Indian Chem. Soc. 28, 257 (1951).

[16] R. Belcher, A. Sykes, and I.C. Taltow, Analyt. chim. acta 10, 34 (1954).

[17] R.B. Hahn and L. Weber, Analyt. Chem. 28, 414 (1956).

[18] V.M. Peshkova, N.V. Mel'chakova, and A.B. Urazbekova, Vestnik Moskva Univ. (in the press).

[19] R.E. Oesper and I.I. Klingenburg, Analyt. Chem. 21, 1509 (1949).

[20] F. Feigl, Chemistry of Specific, Selective, and Sensitive Reactions (New York, 1949) p. 213.

[21] R.B. Hahn and L. Weber, J. Am. Chem. Soc. 77, 4777 (1955).

[22] R.B. Hahn and P.I. Joseph, J. Am. Chem. Soc. 79, 1298 (1957).

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COLOR AND FLUORESCENT REACTIONS FOR GALLIUM

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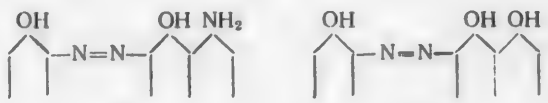
Dyes which had been synthesized by coupling diazo compounds obtained from o-aminophenol and its derivatives, with H-acid [1, 2], were suggested recently as reagents for gallium. The most valuable of these proved to be the reagent which has been called "gallion" [2-3]. It should be pointed out that the reagents suggested have not yet been studied in sufficient detail. Thus, we have not found any information on the effect of pH on the sensitivity, nor any results on the composition of the compounds formed; their use in quantitative analysis, e.g., as complexonometric indicators, etc., has been studied to a comparatively small extent.

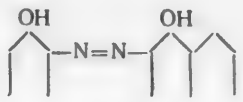
Bearing in mind the comparatively small number of known reagents for gallium, we thought that a more detailed study of the reagents indicated might be of undoubted interest. At the same time, we investigated some other dyes differing in composition from gallion.

The dyes studied contained the following atomic groups:



(I)

(II)



(III)

It is not difficult to see that there are two hydroxy groups in the o,o' position to the azo group in all the dyes studied. This determines their capacity to react with gallium salts. However, the presence (or absence) of a hydroxy or amino group in the peri position with respect to the ortho hydroxy group leads, as we shall see below, to some characteristic properties in the reaction products formed.

The experiments were carried out on a semimicro scale as follows. To 0.1 ml of gallium nitrate solution (0.1 mg Ga^{3+}) was added 0.1 ml of a buffer solution with a definite pH,* 1-2 drops of a 0.1% aqueous solution of the dye, and any color or fluorescence** which developed on heating to 60-70° observed. A control test was carried out at the same time. Of 68 dyes tested, 22 gave positive reactions for gallium. It was found possible to divide all the reagents into two groups.

The first group includes those reagents which, on interacting with a solution of a gallium salt, form brightly colored compounds. Reagents containing group (I) (Table 1, reagents 1-5) belong to this group.

The second group includes those reagents which give with gallium not only colored, but fluorescent reaction products. These reagents contain atomic groups (II) and (III) (Table 1, reagents 6-9). Table 1 contains only

*The acetate or ammoniacal buffer solutions were prepared according to published methods [4, 5].

**Fluorescence was observed on illuminating with a mercury quartz lamp provided with a UFS-3 black filter.

TABLE 1

Color and Fluorescent Reactions for Gallium

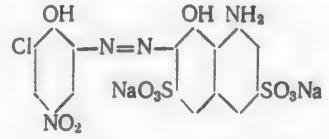
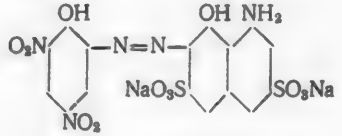
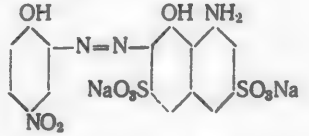
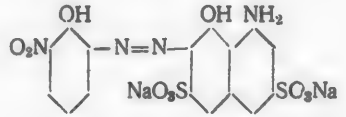
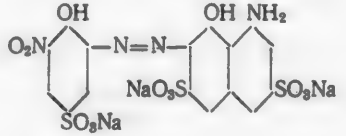
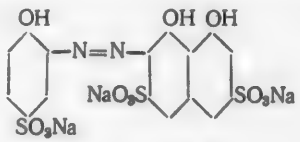
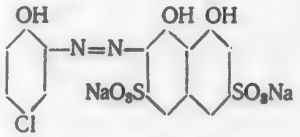
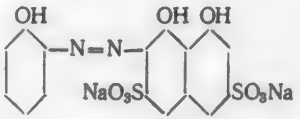
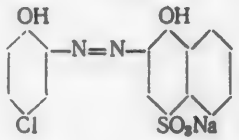
Dye No.	Name	Formula	pH	Color		Fluorescence		Limiting concentration
				control	gallium	control	gallium	
1	Gallion		2—3 4—6	Rose Violet	Pale blue Blue	— —	— —	1 : 1 000 000 1 : 400 000
2	Acid chrome dark-green		3—5	Rose-violet	Blue	—	—	1 : 800 000
3	Palatin chrome green		3—6	Rose	Pale blue	—	—	1 : 800 000
4*	—		2—3 4—6	Rose Violet	Pale blue Blue	—	—	1 : 800 000
5*	—		2—3 4—6	Rose Violet	Pale blue Blue	—	—	1 : 1 000 000

TABLE 1 (continued)

6	Acid chrome blue K		4—8	Red	Violet-red	Violet	Red	1 : 1 000 000
7	Acid chrome dark-green		3—5	Red	Violet	Violet	Red	1 : 700 000
8	Direct blue B		3—5	Red	Violet	Violet	Red	1 : 600 000
9	Acid chrome dark blue 3K		1—5	Red	Violet-red	Red	Bright-rose	1 : 800 000

*Reagents 4 and 5 do not possess arbitrary names.

TABLE 2

Color Reactions of Some Cations

Dye No.	pH	Control	Cations								
			Ga^{3+}	In^{3+}	Y^{3+}	Th^{4+}	Zn^{2+}	Co^{2+}	Al^{3+}	Sc^{3+}	La^{3+}
			Color observed								
1	2	Rose	Pale blue	—	—	Violet	—	—	Blue	Violet	—
	3	"	"	Violet	—	"	—	—	"	"	—
	4	Violet	Blue	Blue	—	" "	—	—	" "	" "	—
	5	"	"	"	Red	" "	—	—	" "	Violet-blue	—
	6	" "	" "	" "		" "	Red	Red	" "		—
2	3	Rose-violet	Blue	—	—	—	—	—	—	Violet with a blue tint	—
	4	"	"	Violet	—	Violet-blue	—	—	—		
	5	" "	" "	Blue							
3	3	Rose	Pale blue	—	—	—	—	—	—	Violet	—
	4	"	"	Blue	—	Red	—	—	—	—	—
	5	" "	" "	"	—	"	—	—	—	Blue	—
	6	" "	" "	" "		Violet	Red	—	Violet	"	—
4	2	Rose	Pale blue	—	—	—	—	—	—	Violet	—
	3	"	"	—	—	Violet	—	—	—	"	—
	4	Violet	Blue	Blue	—	"	—	—	—	Blue	—
	5	"	"	"	—	Violet with a blue tint	—	—	—	"	—
	6	" "	" "	" "	—		Blue	—	Rose	" "	—
5	2	Rose	Pale blue	—	—	—	—	—	—	Violet with a blue tint	—
	3	"	"	—	—	—	—	—	—		
	4	Violet	Blue	Blue	Violet with a red tint	—	—	Violet with a red tint	—	Blue	Violet with a red tint
	5	"	"	"					Red	"	
	6	" "	" "	" "		—	—			" "	

TABLE 3

Fluorescent Reactions of Some Cations

Reagent No.	pH	Cations						
		control	Ga^{3+}	In^{3+}	Sc^{3+}	Y^{3+}	Al^{3+}	Th^{4+}
6	4	Violet	Rose	—	Red	—	Rose-raspberry	—
	5	"	"	—	—	—	"	—
	6	" "	" "		Red	Red	" "	Red
	7	" "	" "		"	"	" "	"
	8	Red	" "		" "	" "	" "	" "
7	3	Violet	Red	—	—	—	—	—
	4	"	"	—	—	—	—	—
	5	" "	" "	—	—	—	Red	—
8	3	Violet	Red	—	—	—	—	—
	4	"	"	—	—	—	—	—
	5	" "	" "	—	—	—	Red	—
9	1	Red	Rose	—	Red	—	—	—
	2	"	"	—	"	—	—	—
	3	" "	" "	Bright-red	" "	—	—	—
	4	" "	" "	" "	" "	Red	—	—
	5	" "	" "	" "	" "	Bright-red	—	—

TABLE 4

Determination of the Ratio of the Molar Amounts of Gallium and Gallion in Their Reaction Product

Amount of components, μ mole		Ratio Ga^{3+} : gallion	Optical density
Ga^{3+}	gallion		
0.066	0.334	≈1:5	0.13
0.08	0.32	1:4	0.17
0.10	0.30	1:3	0.22
0.133	0.267	~1:2	0.18
0.20	0.20	1:1	0.10

those reagents which permit detection of 0.15 γ of gallium and less in 0.1 ml of solution (i.e., a limiting dilution of 1:600,000 and less). Only the limiting concentrations for the fluorescent reaction are given for reagents 6-9.

It follows from Table 1 that gallium salts react with the dyes indicated mainly at low pH values. Gallion is one of the most sensitive reagents for gallium. However, a similar sensitivity can be attained when the other reagents are used. The advantage of the second group of reagents is their capacity to give fluorescent as well as color reactions.

Lukin and Zavarakina [2] have noted the effect of substituents in the phenol ring on the analytical properties of the reagents obtained. It is not difficult to see that these properties depend to an even greater extent on the nature of the substituents in the naphthalene ring.

We have also studied the interaction of the dyes tested with some other cations (In^{3+}, Y^{3+}, Th^{4+}, Zn^{2+}, Ce^{3+}, Al^{3+}, Sc^{3+}, La^{3+}, Fe^{3+}).

To 0.1 ml (100 γ) of a solution of the salt of the corresponding cation was added 0.1 ml of buffer solution, 1-2 drops of a 0.1% aqueous solution of the dye, and the whole heated to 60-70°; any color or fluorescence which developed was observed (Tables 2 and 3).

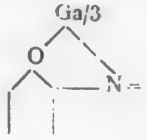
It is clear from Tables 2 and 3 that, of the cations listed above, In^{3+}, Sc^{3+}, and Th^{4+}, and also trivalent iron

are the ones which mainly interfere with the color reaction for gallium. It is interesting to note that, at low pH values, zinc, cerium, yttrium, and lanthanum ions do not form colored compounds with the given reagents.

We determined the ratio of the molar amounts of gallium and gallion in their reaction product at pH 3 by the isomolar series method. For this purpose, we used 10^{-4} M solutions of gallium and the dye. The solutions were mixed in such proportions that the total amount of the components was equal to 0.4 μmole. The total volume of the test liquid, including the buffer solution, was 5 ml in each case, the layer thickness was 1 cm. A control test was carried out at the same time using the same amount of dye so as to take into account the effect of excess reagent on the color of the reaction product. The optical density was measured on the FÉKN-54 photocolorimeter at 610 mμ (Table 4).

Thus, one ion of gallium corresponds to three molecules of dye in the compound formed. Similar tests with other total amounts of gallium salt and gallion led to the same results.

The following formula can, accordingly, be proposed:



We examined the possibility of using the dyes tested as indicators for the complexonometric titration of gallium. Preliminary experiments showed that when a solution of sodium ethylenediaminetetracetate is added to the colored reaction product of gallium with dyes 1, 3, or 5 no color change is observed in the cold. When the solution is heated during titration, a change from blue to rose can be observed.

We standardized the sodium ethylenediaminetetracetate solution by means of a standard solution of a gallium salt.

To 1 ml of a solution of a gallium salt (250 and 350 γ/ml) was added 1 ml of buffer solution (pH 2 in the case of dyes 1 and 5, and pH 3 for dye 3) and one drop of a 0.1% aqueous solution of the dye. The solution was heated to 60-70°, and a 0.01 M solution of sodium ethylenediaminetetracetate added dropwise from a microburet until the color changed.

TABLE 5

Standardization of Sodium Ethylenediaminetetracetate Solution

Dye No.	Amt sodium ethylenediaminetetracetate solution used for titrating gallium, ml		Factor of the sodium ethylenediaminetetracetate as established by means of gallium, mg ml	
	0.35 mg Ga^{3+}	0.25 mg Ga^{3+}		
1	1,05	0,74	0,33	0,34
3	1,07	0,75	0,33	0,33
5	1,08	0,76	0,32	0,30
			Mean	0,33

Thus, under the conditions used, 1 ml of sodium ethylenediaminetetracetate solution corresponds to 0.33 mg gallium (Table 5). These results agree completely satisfactorily with the calculated (theoretical) titer of the sodium ethylenediaminetetracetate as determined against gallium. For determination of 25 γ/ml Ga^{3+} and less we used a solution of sodium ethylenediaminetetracetate which had been diluted ten times. Results for the determination of the gallium content in the test solutions are given in Table 6.

The results obtained show that dyes 1, 3, and 5 can be used as indicators for the complexonometric titration of gallium.

It should be noted that, when Sc^{3+}, Al^{3+}, Zn^{2+}, In^{3+}, and Fe^{3+} are present in solution they interfere with determination of gallium. Thus, complexonometric titration of gallium should be preceded by separation of the latter from the ions listed (e.g., by extraction).

TABLE 6

Complexonometric Determination of Gallium

Ga^{3+} taken, γ/ml	Dye number								
	1	3	5	1	3	5	1	3	5
	amt.sodium ethylenediaminetetracetate solution used for titration, ml			Ga^{3+} found, γ/ml			experimental error, %		
300	0,91	0,90	0,91	301	298	301	0,33	0,66	0,33
200	0,6	0,6	0,61	198,5	198,5	202	0,75	0,75	1
100	0,3	0,31	0,31	99	102,5	102,5	1,0	2,5	2,5
52	0,16	0,15	0,15	53	49,6	53	1,9	4,6	1,9
25	0,78	0,76	0,75	25,7	25,1	24,8	3	0,4	0,8
15	0,45	0,42	0,45	15	14	15	0	6,6	0
10	0,33	0,3	0,27	11	10	9	10	0	10
5	0,15	0,18	0,17	5	6,0	5	0	20	10

SUMMARY

A number of dyes have been suggested as sensitive reagents for gallium.

It has been shown that some of these dyes form colored as well as fluorescent reaction products.

The composition of the compound formed between gallium and gallion has been determined.

It has been shown that some of these dyes can be used as indicators for the complexonometric microdetermination of gallium.

LITERATURE CITED

[1] A.M. Lukin, G.G. Karanovich, G.B. Zavarikhina, and P.A. Ionova, Theses of Reports Given at the First All-Union Conference on the Use of Organic Reagents in Analytical Chemistry [in Russian] (Izd. AN SSSR, Moscow-Leningrad, 1956) p. 64.

[2] A.M. Lukin and G.B. Zavarikhina, Zhur. Anal. Khim. 13, 66 (1958).*

[3] D.P. Shcherbakov and A.I. Ivankova, Zavodskaya Lab. 24, 667 (1958).

[4] T.S. Britton, Hydrogen Ions [Russian translation] (ONTI, 1936) p. 208.

[5] A.K. Babko and A.T. Pilipenko, Colorimetric Analysis [in Russian] (Goskhimizdat, Moscow, 1951) p. 338.

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A NEW REAGENT FOR THE LUMINESCENT DETERMINATION OF GALLIUM

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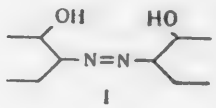
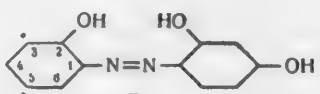
It has been shown in a previous article that the introduction of certain substituents into the molecule of a o,o'-dihydroxyazo compound, which itself has no analytical significance, can convert this compound into a valuable colorimetric reagent. Accordingly, we thought it would be of interest to establish how true this is for luminescent reagents. The opinion has been expressed that a substituent introduced into an organic molecule which can luminesce, can, in most cases, lead to extinction of the luminescence [2]. For example, F, Cl, Br, and I decrease the intensity of the fluorescence of aromatic compounds in the order indicated [3, 4]. The NO_2 group extinguishes fluorescence strongly, and, in almost all cases, leads to its disappearance. In accordance with the views advanced by Lewis and Calvin [2], one might even conclude that the fluorescence in substituted compounds should be less clearly expressed than in unsubstituted compounds.

We could not use a number of compounds obtained earlier [1] for solving the problem confronting us, since, on account of steric hindrance connected with the presence of the sulfo group in the ortho position with respect to the azo group, one could not expect that their complexes with gallium [5] would fluoresce; this assumption was confirmed experimentally. As a consequence, we decided to concentrate on another series of compounds containing group (I), i.e., on those compounds which are obtained by coupling the diazo components obtained from



I



II

o-aminophenol and its derivatives with resorcinol [formula (II), Table 1]. As substituents, we used the same groups in the same positions with respect to the hydroxy group as before [1]. These positions are marked with asterisks in formula (II) (positions 3 and 5). Synthesis of the azo compounds does not present any difficulties, so that there is no need to describe them. All the compounds obtained were purified by various techniques to a chemically pure state. Twelve azo dyes were prepared in all.*

All the materials synthesized are compounds which possess a flexible structure; fluorescence develops in them as a result of the clearing of internal radiationless transitions during the formation of inner-complex compounds with cations [6]; we are of the opinion that, in this case, some substituents can favor an increase in the fluorescence of the complexes.

The sensitivity of detection of gallium by means of all these compounds was established directly in aqueous solution, and after extraction of the complex formed with an equal volume of isoamyl alcohol. The optimum pH of the solution [1, 9], which was 3.5, was established by adding a phthalate buffer solution [8]. 0.2 ml of a 0.01% solution of the reagent in acetone was added to 10 ml of test solution. Fluorescence spectra were taken in parallel for solutions containing 0.5 γ gallium. The fluorescence spectra were taken by means of a UM-2 monochromator and a FÉU-19 photomultiplier. The fluorescence of the solutions was excited by light from a PRK-2 mercury-quartz lamp fitted with a UFS-3 filter.

*G.B. Zavarikhina and N.S. Sysoeva took part in the syntheses of the compounds indicated.

TABLE 1

Characteristics of the Fluorescence Reactions Which Develop During the Interaction of Azo Dyes Obtained from Resorcinol [formula (II)] with Gallium Cations

Test No.	Substituent in the positions given in formula II		Sensitivity (γ Ga in 5 ml)	
	3	5	in aqueous solution	in isoamyl alcohol
1	H	H	0.4	0.05
2	H	Cl	0.6	0.1
3	SO_3H	Cl	0.01	0.005
4	NO_2	Cl	–*	–
5	H	NO_2	–	0.01
6	SO_3H	NO_2	–	0.003
7	NO_2	NO_2	–	–
8	Cl	NO_2	–	0.1
9	H	SO_3H	0.05	–
10	SO_3H	SO_3H	0.02	–
11	NO_2	SO_3H	–	–
12	Cl	SO_3H	0.1	–

*The asterisk indicates absence of fluorescence for amounts of gallium up to 1.0 γ.

To supplement published results [5-7], it was established that all the compounds tested do not fluoresce when gallium is absent. When gallium is present, some of them give interaction products which can fluoresce.

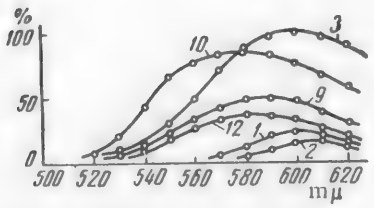


Fig. 1. Fluorescence spectra of aqueous solutions of the compound of gallium with trihydroxyazo compounds. The number on the curves corresponds to the number of the compound in Table 1. The intensity of the fluorescence as compared with the fluorescence of compound 3 at 600 mμ taken as 100%, is plotted along the ordinate.

It follows from the results obtained (Table 1 and Figs. 1 and 2) that the nature, number, and position* of the substituents introduced have an essential influence on the probability of internal radiationless transitions in the molecules of the inner-complex compounds of the gallium cation with the trihydroxy azo compounds tested, which leads, not only to an increase in this probability, but even to its decrease. Accordingly, the introduction* of substituents, as in the case of colorimetric reagents [1], can lead to the creation of valuable luminescent reagents from similar unsubstituted compounds which have no practical importance.

The nitro group, whatever its position, extinguishes the fluorescence of the inner complex compound in aqueous solution; in isoamyl alcohol, however, the same group, but only in the para position, can lead to a significant increase in the intensity of the fluorescence (compounds 1, 5, 6, and 8).

In the absence of a nitro group, the sulfo group in the para position leads to an increase in the fluorescence in aqueous solution, and to its extinction in isoamyl alcohol (compounds 1, 9, 10, and 12); in the ortho position, the sulfo group behaves differently, depending on the nature of the substituent in the para position (compounds 3, 6, and 10).

The compound of gallium with the mono chloro derivative has a lower intensity of fluorescence, and has a

*All references to the position of substituents given in the text below are given with respect to the hydroxy group of the diazo component.

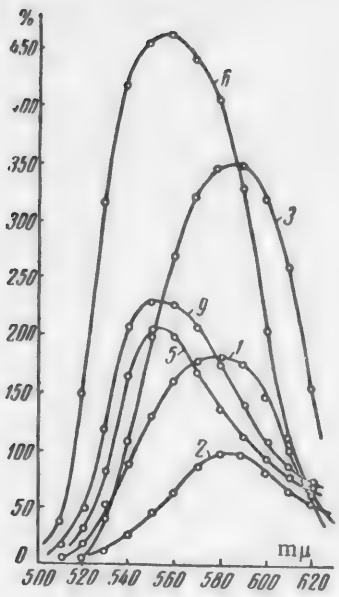
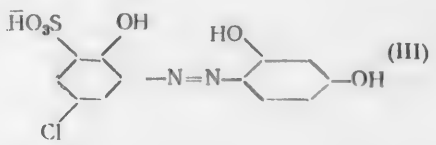


Fig. 2. Fluoresence spectra of the compound of gallium with trihydroxy-azo and isoamyl alcohol. The numbers on the curves correspond to the number of the compound in Table 1. The intensity of the fluorescence is given to scale, as is shown in Fig. 1.

spectrum which is shifted toward the long wave side, both in aqueous solution and in isoamyl alcohol (compounds 1 and 2). Additional introduction of a sulfo group into the mono chloro derivative (compound 7), in the ortho position, leads to a reagent whose compound with gallium has a maximum intensity of fluorescence in aqueous solution. Switching these substituents (compound 12) strongly depresses both the sensitivity and the intensity of the fluorescence.

Thus, the combined effect of two substituents cannot be regarded as the sum of the two taken separately. The same conclusion follows from a comparison of the compounds 2, 3, 9, and 10. This conclusion also holds true for the effect of a substituent on the fluorescent properties of the compounds tested, as on the colorimetric properties of compounds studied earlier [1].

Of the greatest interest as a luminescent reagent for gallium is compound 3* (III).



(III)

Although the product formed by the interaction of gallium with compound 6 exhibits a somewhat higher intensity of fluorescence on extraction with isoamyl alcohol, in aqueous solution, however, it does not luminesce. The compound which we chose, namely, 2,2',4'-trihydroxy-5-chloro-1,1'-azobenzene-3-sulfonic acid luminesces in both media on interacting with gallium.

The optimum pH value for development of a luminescent reaction with gallium is 1.7-4.0 both in aqueous solution, and on extraction with isoamyl alcohol. When equal volumes of aqueous solution and isoamyl alcohol are used, the intensity of the fluorescence of the extracted complex is 3.5 times that in the aqueous solution, irrespective of the pH. The reaction sensitivity, both for visual observations of the fluorescence, and when a monochromator with a photomultiplier is used, is 0.01 γ Ga in 5 ml in aqueous solution, while on extracting the complex with isoamyl alcohol (the volume of which is equal to the volume of the aqueous solution), the sensitivity is 0.005 γ Ga in 5 ml. The time taken for maximum fluorescence to develop (for amounts of gallium not exceeding 0.05 γ in 5 ml) is 50-60 minutes, while for amounts of gallium ranging from 0.05-0.5 γ in 5 ml, the time is 25-30 minutes. The intensity of the fluorescence is linearly related to a gallium concentration of up to 0.5 γ in 5 ml of solution, both for the aqueous solution and for the isoamyl alcohol extract.

At pH 2.0-3.0, the fluorescence does not decrease in the presence of Li, Na, K, Cs, NH_4, Ag, Zn, Cd, Hg, Be, Mg, Ca, Sr, Ba, Tl, In, Ge, Pb, As, Sb^{III}, Sb^{IV}, Bi, Cr, Se, Te, Mn, Ru, Co, Th, Nd, Ce, Pr, Ni, Cl^-, NO_3^-, SO_4^{2-}, phthalates, citrates, and acetates, in amounts of 50 γ in 5 ml. Sn, Zr, and Pd in amounts less than 5 γ in 5 ml of solution do not extinguish the luminescence, while Cu, Fe^{III}, Fe^{II}, V, and Mo in amounts less than 0.5 γ in 5 ml of solution do not extinguish the luminescence.

Of the ions listed which, in amounts less than 50 γ in 5 ml of solution, do not decrease the fluorescence, only aluminum gives a fluorescence; however, this fluorescence is considerably less intense than that of gallium. For a ratio of gallium to aluminum of 1:1, the latter can be disregarded and measurements are carried out at pH 1.7-3.5. When the amount of aluminum present is ten times that of gallium, interference from aluminum can be removed by establishing a pH of 1.7-2.7, while, when the amount of aluminum is one hundred times that of gallium, it is necessary to work within an even narrower range (pH 1.7-2.2).

*This reagent is produced commercially under the name "lumogallion IREA."

2,2',4'-Trihydroxy-5-chloro-1,1'-azobenzene-3-sulfonic acid is a more sensitive and selective reagent for gallium than acid chrome blue-black [10-12] or sulfonaphtholresorcinol [13-15]. Of the large number of dihydroxyazo compounds tested as reagents for the luminescent determination of gallium [10-18], hitherto no compound was known which formed a complex with gallium which fluoresces both in aqueous solution and on extraction with an organic solvent.

We used 2,2',4'-trihydroxy-5-chloro-1,1'-azobenzene-3-sulfonic acid [20] for determining gallium in selenium. 100 mg of selenium was weighed out to an accuracy of 1 mg and carefully ground in an agate mortar; it was transferred to a platinum basin and dissolved on gentle warming in 3 ml of nitric acid which had been distilled in a quartz apparatus. The solution was evaporated to dryness without boiling the nitric acid. The dry residue of selenium dioxide was dissolved in 4 ml of distilled water, and the solution neutralized with ammonia to pH 3.0-3.5 using universal indicator paper; this solution was transferred to a 20-ml standard flask. The platinum basin was washed twice with 5 ml of a buffer solution with a pH of 3.0, and the washings added to the standard flask, and the volume made up to the mark with the same solution. After the solution had been mixed, 5-ml aliquots were transferred into four test tubes; into one of these test tubes was added 0.1 ml of a standard solution of gallium containing 1.0 γ/ml Ga, while into another was introduced 0.1 ml of another standard solution containing 0.1 γ/ml Ga; into a third test tube was added 0.1 ml of a 0.01 N solution of sodium ethylenediaminetetracetate, and into a fourth, 0.1 ml of distilled water. 0.2 ml of a 0.01% solution of the reagent in acetone was added to each of the four test tubes, and the solutions allowed to stand for one hour to one hour, twenty minutes. The relative intensity of these solutions was then measured in a 6-ml cuvette (illuminated with ultraviolet) using a UM-2 monochromator and a FÉU-19 photomultiplier. The percentage content of the gallium in the test sample (a) was calculated by means of the formula:

$$a = \frac{\Delta C_{Ga}(I_x - I_T)}{(I_{Ga} - I_x)n \cdot 2500}\ \%,$$

where ΔC_{Ga} is the amount of gallium introduced in γ; n is the weight of the selenium sample taken in g; I_X is the relative intensity of the fluorescence of the test sample; I_{Ga} is the intensity of the fluorescence of the solution to which gallium has been added; I_T is the reading for the blank solution (with sodium ethylenediaminetetracetate).

For gallium contents less than $5 \cdot 10^{-5}$%, 2.5 ml of isoamyl alcohol is added to each of the test tubes containing the test solution, the sodium ethylenediaminetetracetate, and the added gallium (to 0.01γ), and after shaking, and allowing the layers to separate out, the intensity of the fluorescence of the extracts measured in a 2.5-ml cuvette.

TABLE 2

Determination of Gallium in Selenium

Weight of Se sample, g	Ga added in γ	Ga found, γ in 5 ml	Content, %		Error, %
			calc.	found	
0,106	0,000	0,003	—	$1,1 \cdot 10^{-5}$	—
0,114	0,05	0,018	$5,5 \cdot 10^{-5}$	$6,3 \cdot 10^{-5}$	+15
0,122	0,05	0,017	$5,3 \cdot 10^{-5}$	$5,6 \cdot 10^{-5}$	+ 6
0,104	0,10	0,026	$1,1 \cdot 10^{-4}$	$1,0 \cdot 10^{-4}$	— 9
0,094	0,10	0,024	$1,2 \cdot 10^{-4}$	$1,02 \cdot 10^{-4}$	—15
0,124	0,20	0,048	$1,7 \cdot 10^{-4}$	$1,5 \cdot 10^{-4}$	—12
0,111	0,20	0,050	$1,9 \cdot 10^{-4}$	$1,9 \cdot 10^{-4}$	0

Results for the determination of gallium in selenium are given in Table 2, from which it is clear that the experimental error does not exceed 15%.

The suggested reagent is also suitable for the purification of the solutions of a number of salts from micro amounts of Al, Cu, Fe, etc., present as impurities, by sorbing their inner-complex compounds by means of activated charcoal or with anion exchange resins [19]. For example, an acetate buffer solution with a pH of 6.0 can be purified from aluminum in contents up to $5 \cdot 10^{-8}$%.

It should be pointed out that the reagent suggested exhibits its highest efficiency (complete absence of fluorescence of the reagent itself under the analytical conditions used) after a special acid purification. Accordingly, a description is given below of the synthesis and purification of the reagent.*

Synthesis of the reagent. 2.2 g of resorcinol with a m.p. of 110° is dissolved in 60 ml of a 10% solution of sodium carbonate. To this solution is added a solution of the diazo compound obtained as follows: 4.4 g of pure 2-amino-4-chlorophenol-6-sulfonic acid is added to 30 ml of water and acidified with 2-3 drops of hydrochloric acid, the solution is diazotized with a solution of 1.4 g of sodium nitrite in 10 ml of water, the progress of the reaction being controlled with starch iodide paper and congo paper.

As the solution of the diazo compound is added, the reaction mass becomes red. After coupling is complete and the mass has been allowed to stand for 2-3 hours, it is acidified with hydrochloric acid; at this stage, a reddish-orange amorphous precipitate separates out. The latter is filtered off and transferred into 150 ml of water and the whole then heated almost to the boiling point; to the hot suspension is added 20 ml of concentrated hydrochloric acid; the orange needles formed (visible under the microscope) are filtered in the hot state, and again transferred into a mixture of 50 ml of water and 20 ml of concentrated hydrochloric acid; the suspension is again heated to the boil and filtered in the hot state, after which the material is dried to constant weight at 80-90°.

$C_{12}H_{10}O_6N_2SCl$. Calculated %: Cl 10.29; S 9.30. Found %: Cl 10.41, 10.51; S 9.27, 9.09.

SUMMARY

A study has been made of the effect of substituents on the luminescent properties of the compounds of gallium with trihydroxyazo compounds obtained by coupling resorcinol with the diazo component from o-aminophenol and its derivatives.

Of the substituted derivatives studied, the most promising as a reagent for the luminescent determination of gallium is 2,2',4'-trihydroxy-5-chloro-1,1'-azobenzene-3-sulfonic acid.

LITERATURE CITED

[1] A.M. Lukin and G.B. Zavarikhina, Zhur. Anal. Khim. 13, 66 (1958).**

[2] C.N. Lewis and M. Calvin, Chem. Rev. 25, 273 (1939).

[3] H. Ley and K. Engelhardt, Z. Phys. Chem. 74, 30 (1910).

[4] L Stark and W. Steubing, Phys. Z. 9, 486 (1908).

[5] E.A. Bozhevol'nov, Trudy IREA (Vsesoyuz. Nauch. Issled. Inst. Khimich. Reaktivov) 23, 147 (1959).

[6] E.A. Bozhevol'nov and A.M. Lukin: Reports and Communications at the VIIIth Mendeleev Session, Anal. Chem. Section, No. 3 (Izd. AN SSSR, Moscow-Leningrad, 1958) p. 87.

[7] C.D. Freeman and C.E. White, J. Am. Chem. Soc. 78, 2678 (1956).

[8] É. Mislovitser, Determination of Hydrogen Ion Concentration in Liquids [in Russian] (NKhTI, 1930).

[9] G.G. Karanovich, L.A. Popova, and B.L. Podol'skaya, Zhur. Anal. Khim. 13, 439 (1958).**

[10] G. Charlot, Analyt. Chim. Acta 1, 218 (1947).

[11] G. Charlot and R. Gauguin, Dosages Colorimetriques (Masson, Paris, 1952) p. 164.

[12] A. Weissler and C.E. White, Ind. Eng. Chem. Anal. Ed. 18, 530 (1946).

[13] V.A. Nazarenko and S.Ya. Vinkovetskaya: Materials of the First Conference of Laboratory Workers MTsM SSSR, Information No. 194, 147, 1956.

[14] V.A. Nazarenko and S.Ya. Vinkovetskaya, Zhur. Anal. Khim. 13, 327 (1958).**

[15] N.S. Poluéktov and N.N. Kiseleva, Zhur. Anal. Khim. 13, 555 (1958).**

*The conditions used for carrying out the synthesis and purification were developed by G.B. Zavarikhina.

**Original Russian pagination. See C.B. translation.

[16] J.A. Radley, Analyst 68, 369 (1943).

[17] L.M. Ladenbauer, J. Korkisch and F. Hecht, Mikrochim. Acta 5-6, 1076 (1955).

[18] V. Patrovsky, Chem. listy 48, 537 (1954).

[19] E.A. Bozhevol'nov, A.M. Lukin, V.M. Yanishevskaya, and E.V. Kholod, Author's Thesis 119287, September 2, 1958.

[20] A.M. Lukin, E.A. Bozhevol'nov, and M.N. Gradinarskaya, Author's Thesis 116838, May 13, 1958.

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SEPARATION OF INDIUM AND GALLIUM BY MEANS OF DIETHYLDITHIOCARBAMATE

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Comparatively few methods have been suggested for the separation of indium and gallium [1-8]. The methods suggested include methods based on extraction with organic solvents [1, 7, 9-13] and chromatographic methods [14-19]. In practice, indium and gallium are separated almost exclusively by the cupferron method, and by extraction of gallium chloride with ether [2, 9]. Other methods do not give reliable results, are characterized by difficulties in carrying them out, and, in some cases, the methods have not been developed sufficiently. Accordingly, there is need for simple, accurate, and reliable methods of separating elements which are as similar in properties as indium and gallium. We have established that under certain conditions it is possible to separate indium and gallium successfully by means of sodium diethyldithiocarbamate.

Sodium diethyldithiocarbamate forms sparingly soluble precipitates with indium and gallium, and also with elements which give stable sulfides in aqueous solution. Indium is quantitatively precipitated at pH 1.5-9, but is not precipitated from HCl (1:1), and from concentrated HCl [20]. During the gravimetric determination of indium in the form of $[(C_2H_5)_2NCS_2]_3In$, it is precipitated with sodium diethyldithiocarbamate at a pH of 4-5, and the precipitate dried at 105° [21, 22]. Patrovskii [23] precipitated indium with sodium diethyldithiocarbamate at pH 7-11 from a solution containing tartrate and cyanide. Thus, it is possible to determine indium in the presence of Al, Ga, Cu, Zn, Cd, and Sn. Indium diethyldithiocarbamate is quantitatively extracted with ethyl acetate at pH 3 [20]. Bode [24] established that indium diethyldithiocarbamate is almost completely extracted with carbon tetrachloride at pH 5-10 from a solution containing tartrate. Potassium cyanide does not affect the extraction. Sodium ethylenediaminetetracetate interferes with the extraction (at pH > 7, indium diethyldithiocarbamate is not extracted at all; at pH 5-7, it is extracted partially). A solution of indium diethyldithiocarbamate in CCl_4 absorbs light in the ultraviolet; the absorption maximum is observed at 305 mμ. It has been suggested that it should be possible to determine indium photometrically by converting the colorless compound $[(C_2H_5)_2NCS_2]_3In$ into the colored compound $Cu[(C_2H_5)_2NCS_2]_2$ [23, 24]. Other disubstituted dithiocarbamates also precipitate indium [25]. This is used, for example, for concentrating traces of indium [26].

Gallium is precipitated by sodium diethyldithiocarbamate at pH 1.5-6 in the form of a white precipitate which is soluble in ethyl acetate [20]. Gallium diethyldithiocarbamate is quantitatively extracted with ethyl acetate at pH 3 [20]. During a study of the interaction of dithiocarbamic acid and its disubstituted salts with the salts of Al, Ga, and In, it was established that aluminum does not give a diethyldithiocarbamate, gallium gives a readily hydrolyzed diethyldithiocarbamate, while indium diethyldithiocarbamate is stable in the presence of water [25].

Bode [24], while studying the behavior of sodium diethyldithiocarbamate toward various elements, established that gallium diethyldithiocarbamate is only extracted with CCl_4 at pH < 5.5, at which value the reagent itself starts to break down. Sodium ethylenediaminetetracetate interferes with the precipitation and extraction. Bode came to the conclusion that sodium diethyldithiocarbamate is not suitable for the quantitative determination of gallium or for its separation from other elements. Some authors have indicated that sodium pyrollidinedithiocarbamate is more suitable for determining gallium and for separating it from other elements [26, 27]. The fact that gallium pyrollidinedithiocarbamate can be extracted at pH 4.8 with chloroform is used for concentrating gallium [26]. A method has been developed for the gravimetric and nephelometric determination of gallium by means of sodium pyrollidinedithiocarbamate [28].

Solutions and reagents. 1. Solutions of gallium and indium nitrates were prepared by dissolving the spectrographically pure metals in the minimum amount of concentrated HNO_3. After dilution with water, the pH of the solution was 1-2. The solutions were standardized by the hydroxyquinoline method [29]. 1 ml of solution contained about 1 mg of Ga and 2.5 mg of In.

2. A 2% aqueous solution of sodium diethyldithiocarbamate "pure" grade.

3. Buffer solutions were prepared by the usual method [30]:

0,2*M* CH_3COOH + 0,2*M* CH_3COONa,	pH 3,72—5,57,
0,2*M* KCl + 0,2*M* HCl,	pH 1,00—2,20,
0,2*M* H_3BO_3 + 0,05*M* $Na_2B_4O_7$,	pH 7,09—9,11.

Interaction of Gallium and Indium Ions with Sodium Diethyldithiocarbamate, and the Properties of the Compounds Formed

The white precipitate formed on addition of sodium diethyldithiocarbamate to a solution of gallium nitrate was filtered off, washed with water, and then heated in a drying oven. It was found that at temperatures above 150° there was observed a sharp decrease in weight; presumably, the precipitate starts to decompose. The gallium and nitrogen content of the precipitate dried at 110-140° to constant weight was determined. In order to determine gallium, the precipitate was treated with HNO_3 (1 : 1) on heating, the solution was evaporated to dryness, and the residue was dissolved in water, and the gallium precipitated with 8-hydroxyquinoline [29]. Nitrogen was determined by the Kjeldahl method.

13.60, 13.82, 13.38, and 13.80% of Ga — an average of 13.65% — and 7.80, 7.89% of nitrogen — an average of 7.85% — was found. The theoretical values for $Ga[(C_2H_5)_2NCS_2]_3$ are 13.55% Ga and 8.17% N. The gallium content of the precipitate was also determined by calcination (carefully at first) of an aliquot at 800-1000°. Quantitative formation of Ga_2O_3 thereupon occurs. 0.2368, 0.2220, and 0.1944 g of the precipitate dried at 110 to 140° were taken; 0.0428, 0.0412, and 0.0356 g of Ga_2O_3 were obtained.

13.38, 13.80, and 13.60% Ga — a mean value of 13.60% Ga — was found, which is in good agreement with the expected amount.

Thus, on mixing solutions of gallium salt and sodium diethyldithiocarbamate, gallium diethyldithiocarbamate is actually formed. After drying at 110-140°, its composition corresponds to the formula $Ga[(C_2H_5)_2NCS_2]_3$.

Gallium diethyldithiocarbamate is soluble in alkalis and ammonia; it is precipitated again from alkali solutions on careful acidification. Acids (HCl, H_2SO_4, and HNO_3) decompose the precipitate. Concentrated acids decompose the precipitate immediately. Concentrated acetic acid in the cold does not affect gallium diethyldithiocarbamate; on heating, it dissolves. Gallium diethyldithiocarbamate is partially decomposed by water on heating; decomposition is particularly significant on boiling. Gallium diethyldithiocarbamate readily dissolves in organic solvents: chloroform, carbon tetrachloride, ethyl acetate, and amyl acetate.

A study of the precipitation of gallium by sodium diethyldithiocarbamate at various pH's was carried out as follows: to a weakly nitric acid solution of gallium nitrate was added a buffer solution in order to establish a definite pH; a 2% aqueous solution of sodium diethyldithiocarbamate was then added in fivefold excess. An indicator was added to control the pH. Since an aqueous solution of sodium diethyldithiocarbamate has a strongly alkaline reaction because of hydrolysis, on addition of this reagent, the pH increases somewhat. The precipitate was filtered off after 30 minutes, washed with water, and dried at 110-140°. The conversion factor to gallium is 0.1355. The pH of the filtrate was determined with a glass electrode.

At pH > 8.5, gallium diethyldithiocarbamate is not precipitated at all. When an alkaline solution (pH > 9) containing gallium and sodium diethyldithiocarbamate is carefully neutralized with acid, then, at pH about 8.3, a precipitate of gallium diethyldithiocarbamate starts to separate out. When gallium diethyldithiocarbamate is precipitated at pH 8-8.3, and alkali or ammonia then added until the pH is greater than 8.3, the precipitate only dissolves partially. As is evident from Table 1, gallium diethyldithiocarbamate is precipitated quantitatively at pH 2.7-5.0. Despite this, determination of gallium as its diethyldithiocarbamate would not seem to be of much practical significance because of the poor selectivity; indium, iron, zinc, and other elements interfere. Tartaric and sulfosalicylic acids do not affect precipitation of gallium diethyldithiocarbamate (Tables 2 and 3) in the pH

TABLE 1

Effect of pH of the Solution on the Precipitation of Gallium Diethyldithiocarbamate*

pH of filtrate	Ga taken, mg	Weight of precipitate, g	Ga found, mg	Error	
				absolute, mg	%
1,06	4,87	0,0204	2,76	−2,11	−43,3
2,00	4,87	0,0280	3,79	−1,08	−22,1
2,67	4,79	0,0358	4,85	+0,06	+ 1,2
3,28	4,77	0,0346	4,68	−0,09	− 1,9
4,60	4,69	0,0342	4,63	−0,06	− 1,2
5,00	4,77	0,0350	4,73	−0,04	− 0,8
5,79	4,77	0,0318	4,31	−0,46	− 9,6
6,00	4,77	0,0316	4,28	−0,49	−10,2
7,00	4,77	0,0290	3,92	−0,89	−18,9
8,00	4,77	0,0262	3,55	−1,22	−25,5

*In all cases, at pH > 4, sodium tartrate was added to the solution to prevent precipitation of gallium hydroxide.

TABLE 2

Effect of Sodium Tartrate on Precipitation of Gallium Diethyldithiocarbamate (pH 4)

Taken				Molar ratio tartrate:Ga	Wt. of precipitate, g	Ga found, mg	Error	
Ga		sodium tartrate					abs., mg	%
mg	mmole per liter	mg	mmole per liter					
5,15	1,84	50	6,4	3,4 : 1	0,0383	5,18	+0,03	+0,6
5,15	1,84	100	12,8	7 : 1	0,0376	5,09	−0,06	−1,2
5,15	1,84	250	32,2	17 : 1	0,0381	5,16	+0,01	+0,2
5,15	1,84	500	64,5	35 : 1	0,0378	5,12	−0,03	−0,6
5,15	1,84	1000	129,0	70 : 1	0,0376	5,09	−0,06	−1,2

TABLE 3

Effect of Sodium Sulfosalicylate on the Precipitation of Gallium Diethyldithiocarbamate (pH 4.4)

Taken				Molar ratio, sulfosalicylate:Ga	Wt. of precipitate, g	Ga found, mg	Error	
Ga		sodium sulfosalicylate					abs., mg	%
mg	mM/liter	mg	mM/liter					
3,86	1,38	60	7,2	5 : 1	0,0282	3,82	−0,04	−1
5,15	1,84	300	36	20 : 1	0,0380	5,14	−0,01	−0,2
5,15	1,84	600	72	39 : 1	0,0378	5,12	−0,03	−0,6
3,87	1,38	1000	121	88 : 1	0,0282	3,82	−0,05	−1,3

range in which precipitation of the latter occurs from the usual solutions. Gallium is precipitated incompletely with sodium diethyldithiocarbamate in the presence of small amounts of sodium oxalate, while in the presence of large amounts of the sodium oxalate it is not precipitated at all (Table 4).

Our experiments confirmed published data [1, 20, 22, 23] on the quantitative precipitation of indium by sodium diethyldithiocarbamate within a wide pH range; tartaric acid does not affect its precipitation. Sulfosalicylic acid and sodium oxalate do not interfere with the quantitative precipitation of indium (Tables 5 and 6).

TABLE 4

Effect of Sodium Oxalate on the Precipitation of Gallium Diethyldithiocarbamate (pH 2.7-5.0)

Taken				Molar ratio, $C_2O_4^{2-}$:Ga	Wt. of precipitate, g	Ga found, mg	Error	
Ga		sodium oxalate						
mg	mmole per liter	mg	mmole per liter				abs., mg	%
2,86	1,08	22,2	4,1	3 : 1	0,0144	1,95	-0,91	— 32
5,15	1,84	59,2	11,04	6 : 1	0,0206	2,79	—2,36	—45,7
5,15	1,84	148,0	27,60	15 : 1	—	—	—	—

TABLE 5

Effect of Sodium Sulfosalicylate on the Precipitation of Indium Diethyldithiocarbamate (pH 4.0). Conversion factor to indium 0.2050

Taken				Molar ratio, sulfosalicylate:In	Wt. of precipitate, g	In found, mg	Error	
In		sodium sulfosalicylate						
mg	mmole per liter	mg	mmole per liter				abs., mg	%
5,92	1,2	400	48,0	40 : 1	0,0288	5,90	—0,02	—0,3
5,92	1,2	800	96,0	80 : 1	0,0282	5,78	—0,14	—2,3
5,33	1,2	800	96,0	80 : 1	0,0257	5,27	—0,06	—1,0

TABLE 6

Effect of Sodium Oxalate on the Precipitation of Indium Diethyldithiocarbamate (pH 3-4)

Taken				Molar ratio, $C_2O_4^{2-}$:In	Wt. of precipitate, g	In found, mg	Error	
In		sodium oxalate						
mg	mmole per liter	mg	mmole per liter				abs., mg	%
5,98	1,3	25,9	4,8	3,7 : 1	0,0293	6,00	+0,02	+0,3
5,98	1,3	52,0	9,6	7 : 1	0,0292	5,98	0,00	0,0
5,98	1,3	122,1	22,8	18 : 1	0,0288	5,90	—0,08	—1,2
5,98	1,3	244,2	45,5	35 : 1	0,0291	5,97	—0,01	—0,2

A Study of the Extraction of Gallium and Indium Diethyldithiocarbamates

Chernikhov and Dobkina [20] have noted that gallium diethyldithiocarbamate is extracted at pH 3 by ethyl acetate. 100 γ out of 120 γ originally taken was found in the ester phase. Gallium diethyldithiocarbamate is also extracted by $CHCl_3$, CCl_4, and other organic solvents. Extraction is carried out best of all with ethyl acetate, the layers separate out rapidly and no foam is formed on the phase boundary, as occurs in the case of $CHCl_3$. We carried out the extraction in a 100 ml separating funnel as follows: to a solution of a gallium salt was added in succession a buffer solution, a 2% solution of sodium diethyldithiocarbamate taken in a fivefold excess, and ethyl acetate; the whole was shaken for two minutes; after separation of the layers, the gallium content was determined by means of 8-hydroxyquinoline. In order to determine gallium, the ester extract was evaporated to dryness on a water bath, the dry residue was then treated with HNO_3 (1:20) and then evaporated to dryness again. The dry residue was dissolved in water and gallium determined. The extractability of indium diethyldithiocarbamate was studied in the same way.

As is evident from Table 7, gallium diethyldithiocarbamate is almost completely extracted with one portion of ethyl acetate at pH 1.5-5. Starting at a pH of 6, more and more of the gallium remains in the aqueous

TABLE 7

Effect of the pH of the Aqueous Solution on the Extraction of Gallium Diethyldithiocarbamate by Ethyl Acetate (the pH of the aqueous solution was measured with a glass electrode)

Acidity of the aqueous solution	Ga taken, mg	Ga found, mg		Extr. Ga	Acidity of the aqueous solution	Ga taken, mg	Ga found, mg		Extr. Ga
		in the ester layer	in the aqueous layer				in the ester layer	in the aqueous layer	
1*N* HCl	3,87	—	3,83	—	pH4,57	3,87	3,86	—	99,7
pH 1,35	5,78	5,40	0,64	93,42	4,70	5,78	5,79	—	100,17
1,61	5,78	5,76	—	99,65	5,86	5,78	4,90	0,71	84,77
2,15	2,90	2,94	—	101,1	6,70	5,78	4,39	1,11	75,95
2,91	5,78	5,83	—	100,56	7,51	5,78	2,99	2,78	51,73
3,85	3,87	3,88	—	100,20	8,15	5,78	0,61	5,15	10,55
4,15	5,78	5,64	0,19	97,57					

TABLE 8

Effect of $Na_2C_2O_4$ on the Extraction of Gallium Diethyldithiocarbamate with Ethyl Acetate (pH 3.4-4)

Taken				Molar ratio, $C_2O_4^{2-}$:Ga	Ga found, mg		% Ga extracted
Ga		sodium oxalate			in the ester layer	in the aqueous layer	
mg	mmole per liter	mg	mmole per liter				
5,78	2,07	33,23	6,20	3 : 1	5,41	0,21	93,59
5,78	2,07	66,50	12,40	6 : 1	3,08	2,44	53,28
5,78	2,07	166,5	31,06	15 : 1	—	5,80	0

TABLE 9

Effect of $Na_2C_2O_4$ on the Extraction of Indium Diethyldithiocarbamate with Ethyl Acetate (pH of the aqueous layer 4)

Taken				Molar ratio, $C_2O_4^{2-}$:Ga	In found, mg		% In extracted
In		sodium oxalate			in the ester layer	in the aqueous layer	
mg	mmole per liter	mg	mmole per liter				
4,74	1,03	18,5	3,4	3 : 1	4,66	—	98,31
4,74	1,03	37	6,8	7 : 1	4,56	—	96,20
4,74	1,03	92,5	17	17 : 1	4,62	—	97,45
7,74	1,03	185	34	34 : 1	4,69	—	98,95

phase, and already, as early as pH > 8, almost all the gallium remains in the aqueous phase. Comparison of the results given in Tables 1 and 7 shows that the pH range for the quantitative precipitation and extraction of gallium diethyldithiocarbamate almost coincide. Tartaric and sulfosalicylic acids do not affect the extraction. Oxalic acid prevents extraction of gallium diethyldithiocarbamate (Table 8).

Our experiments confirmed published data [20, 23] relating to the quantitative extraction of indium diethyldithiocarbamate with one portion of ethyl acetate at a pH of 3-10. Tartaric, sulfosalicylic, and oxalic acids do not interfere with the extraction of indium diethyldithiocarbamate with ethyl acetate.

Technique for Separating Indium and Gallium

A comparison of the results given in Tables 4 and 6, 8 and 9 shows that indium and gallium can be separated at pH 3-5, if the indium diethyldithiocarbamate is precipitated and is extracted with ethyl acetate in the

TABLE 10

Precipitation of Indium with Sodium Diethyldithiocarbamate in the Presence of Gallium (at pH 3-4) on Addition of Excess Oxalate

Taken, mg		Ratio, In:Ga	In found, mg	Error in determining In		Ga found, mg	Error in determining Ga	
In	Ga			abs., mg	relative, %		abs., mg	relative, %
2,39	19,68	1 : 8	2,44	+0,05	+2,1	19,89	+0,21	+1,06
2,39	19,68	1 : 8	2,46	+0,07	+2,9	19,82	+0,14	+0,7
2,99	4,92	1 : 2	2,97	—0,02	—0,7	4,96	+0,04	+0,8
5,98	4,92	1 : 1	5,79	—0,19	—3,1	4,94	+0,02	+0,4
5,98	4,92	1 : 1	5,96	—0,02	—0,3	4,96	+0,04	+0,8
5,98	4,92	1 : 1	6,03	+0,05	+0,8	4,79	—0,13	—2,6
5,98	4,92	1 : 1	6,04	+0,06	+1,0	4,93	+0,01	+0,2
5,98	2,46	2 : 1	6,01	+0,03	+0,5	2,30	—0,16	—3,3
5,98	2,46	2 : 1	5,90	—0,08	—1,3	2,50	+0,04	+0,8

TABLE 11

Separation of Indium and Gallium by Extraction of Indium Diethyldithiocarbamate with Ethyl Acetate in the Presence of Excess Oxalate (pH 3-5)

Taken, mg		Ratio, In:Ga	In found, mg	Error in determining In		Ga found, mg	Error in determining Ga	
In	Ga			abs., mg	relative, %		abs., mg	relative, %
4,74	5,78	1 : 1	4,74	—	—	5,80	+0,02	+0,3
2,84	5,78	1 : 2	2,85	+0,01	+0,4	5,80	+0,02	+0,3
2,94	15,02	1 : 5	3,00	+0,06	+2,0	14,96	—0,06	—0,4
2,94	30,04	1 : 10	2,96	+0,02	+0,7	29,97	—0,07	—0,2

presence of excess sodium oxalate.* To a solution containing 2-6 mg of In and 2.5-30 mg Ga is added sodium oxalate or oxalic acid. For each milligram of In or Ga 20-30 mg of sodium oxalate or oxalic acid is added (15 moles of oxalic acid or sodium oxalate per mole of In or Ga). The solution is neutralized with ammonia, using methyl orange as indicator. A 2% aqueous solution of sodium diethyldithiocarbamate (usually, it is taken in a two- to three-fold excess) is then added with stirring. The solution plus the precipitate of indium diethyldithiocarbamate is allowed to stand for 8-24 hours, and the precipitate then filtered through a No. 3 or No. 4 glass crucible; it is washed with water and dried to constant weight at 105° and weighed. The conversion factor to In is 0.2050. Gallium is determined in the combined filtrates and wash liquors by precipitation with 8-hydroxyquinoline.

Indium and thallium can be separated by an extraction method. 10-30 ml of ethyl acetate is added and the whole shaken for two minutes. The phases are allowed to separate and the ester phase evaporated to dryness on a water bath, the residue is treated with HNO_3 (1:20) and again evaporated to dryness; the dry residue is dissolved in a small volume of water and indium precipitated with 8-hydroxyquinoline. As is evident from Tables 10 and 11, the results obtained during the separation of indium and gallium are completely satisfactory. The average error is 1-2%.

Completeness of separation of the precipitates of indium diethyldithiocarbamate and gallium and indium 8-hydroxyquinolates was investigated spectroscopically. Indium diethyldithiocarbamate was calcined to In_2O_3 at 800-1000°, while indium and gallium 8-hydroxyquinolates were calcined with oxalic acid. The spectra were photographed on an ISP-22 spectrograph, the spectra being excited in an ac arc, while the exposure time was 30 seconds. Examination of the spectra showed that the In content of the Ga_2O_3 was of the order of 10^{-3}%, while the

*According to the results of some authors [31-35], indium and gallium ions form complex ions with oxalate ions.

Ga content of the In_2O_3 was 10^{-2} to 10^{-3}%, i.e., for the amounts of In and Ga taken, the amount of one element present as an impurity in the other is of the order of 0.0001-0.0005 mg. Thus, the fact that accurate results are obtained for indium and gallium is not a result of compensation of errors.

Aluminum does not interfere with the separation of indium from gallium, while iron, both ferrous and ferric, behaves like indium, i.e., sodium oxalate does not interfere with the precipitation and extraction of Fe and In diethyldithiocarbamates. Accordingly, indium will be precipitated and extracted together with iron in the presence of sodium oxalate.

SUMMARY

Gallium diethyldithiocarbamate is precipitated at pH 1-8.5, while at pH 2.7-5.0 the precipitation is quantitative. Gallium diethyldithiocarbamate is extracted quantitatively by ethyl acetate at pH 1.5-5. Tartaric and sulfosalicylic acids do not affect either the precipitation or the extraction. Oxalic acid prevents precipitation and extraction.

Indium diethyldithiocarbamate at pH 3-10 is quantitatively precipitated and quantitatively extracted by ethyl acetate. Tartaric, sulfosalicylic, and oxalic acids do not affect the precipitation and extraction.

A technique has been developed for separating indium and gallium; it is based on precipitation of indium diethyldithiocarbamate, or on its extraction with ethyl acetate at pH 3-5 in the presence of excess oxalate. For ratios of In : Ga up to 1 : 10, the error for In and Ga is ±1-3%.

LITERATURE CITED

[1] A.I. Busev, Analytical Chemistry of Indium [in Russian] (Izd. AN SSSR, Moscow-Leningrad, 1958).

[2] L. Moser and A. Brukl, Monatsh. Chem. 51, 328 (1929).

[3] F.E. Browning and L.E. Porter, J. Am. Chem. Soc. 43, 126 (1921).

[4] L.M. Dennis and J.A. Bridgman, J. Am. Chem. Soc. 40, 1549 (1918).

[5] S. Ato, Sci. Pap. Inst. Tokyo 24, 270 (1934).

[6] A. Tchakirian, Compt. rend. 189, 251 (1929).

[7] I.P. Alimarin and B.N. Ivanov-Émin, Zhur. Priklad. Khim. 9, 1124 (1936).

[8] T.W. Richards and S. Boyer, J. Am. Chem. Soc. 41, 133 (1919).

[9] E.H. Swift, J. Am. Chem. Soc. 46, 2375 (1924).

[10] T.V. Cherkashina, Zavodskaya Lab. 22, 276 (1956).

[11] H.M. Irving and F.J.C. Rossotti, Analyst 77, 801 (1952).

[12] J. Hoste and H. van den Berge, Mikrochim. acta 4-6, 797 (1956).

[13] H. Hartkamp and H. Specker, Angew. Chem. 68, 21, 678 (1956).

[14] D. Jentzsch, Z. analyt. Chem. 150, 4, 241 (1956).

[15] K.A. Kraus, F. Nelson, and G.W. Smith, J. Phys. Chem. 58, 1, 11 (1954).

[16] R. Klement and H. Sandmann, Z. Analyt. Chem. 145, 325 (1955).

[17] T.W. Arden, F.H. Burstall, G.R. Davies, J.A. Lewis, and P.G. Linstead, Nature 162, 691 (1948).

[18] R.G. de Carvalho and M. Lederer, Analyt. Chim. Acta 13, 5, 437 (1955).

[19] S. Kertes and M. Lederer, Analyt. Chim. Acta 15, 6, 543 (1956).

[20] Yu.A. Chernikhov and B.M. Dobkina, Zavodskaya Lab. 15, 1143 (1949).

[21] F. Ensslin, Metall und Erz 38, 305 (1941).

[22] F. Ensslin and H. Dreyer, Z. Anorg. Allgem. Chem. 249, 132 (1942).

[23] V. Patrovsky, Chem. listy 48, 7, 1047 (1954).

[24] H. Bode, Z. Analyt. Chem. 144 (3), 165 (1955).

[25] M. Delepine, Ann. Chimie 6, 636 (1951).

[26] A. Stetter and H. Exler, Naturwissenschaften 42, 45 (1955).

[27] K. Gleu and R. Schwab, Angew. Chem. 62A, 320 (1950).

[28] W. Geilmann, H. Bode,and E. Kunkel, Z. Analyt. Chem. 148 (3), 161 (1955).

[29] R. Fresenius and G. Jander, Handb. Analyt. Chem. 3, 545, 586 (1944).

[30] E.N. Vinogradov, Methods of Determining Hydrogen Ion Concentration [in Russian] (Izd. MGU, 1956) pp. 88-89.

[31] T. Moeller, J. Am. Chem. Soc. 62, 2444 (1940).

[32] S. Lacroix, Ann. chimie (12), 4, 5 (1949).

[33] É.N. Deichman, Zhur. Neorg. Khim. 3, 1592 (1958).

[34] G.S. Savchenko, Chemistry of the Rare Elements [in Russian] 3, 57 (1957).

[35] N.K. Dutt and B. Sur, Z. Anorg. Allgem. Chem. 293, 195 (1957).

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DETERMINATION OF RARE EARTHS PRESENT AS IMPURITIES IN SAMARIUM AND EUROPIUM

V.L. Kustas and G.V. Lazebnaya

The present article contains a description of a method for the quantitative determination of rare-earth elements and yttrium present as impurities in pure samarium and europium oxides. There is very little published data on the analysis of europium and samarium. Tassel [1, 2] has developed a technique for the determination of europium and samarium on a spectrograph with the high dispersion of 2.5 A/mm.

Kryuger and Shvangiradze [3] analyzed samarium for europium using the ISP-22 spectrograph, which has average dispersion.

For production control, a technique is required for the total quantitative analysis of europium and samarium oxides for their content of all the rare earths and yttrium. Such a technique should not only be sufficiently sensitive and accurate, and should not require a large amount of the very pure oxides of the rare earths, but the time taken to carry out an analysis should also be as short as possible. The purpose of the work described here was to develop such a method. In order to cut down on the time taken, the analysis is carried out in two stages: the elements of the cerium group are determined simultaneously in samarium and europium, while the elements of the yttrium group are also determined simultaneously. The method described below is applicable in the concentration range from the limit of detection to 5%.

The method chosen was emission spectrographic analysis from solutions. A drop of test solution was placed on the end of a graphite electrode which had been treated beforehand with a 3% solution of polystyrene in benzene, and the whole dried at 100° [4].

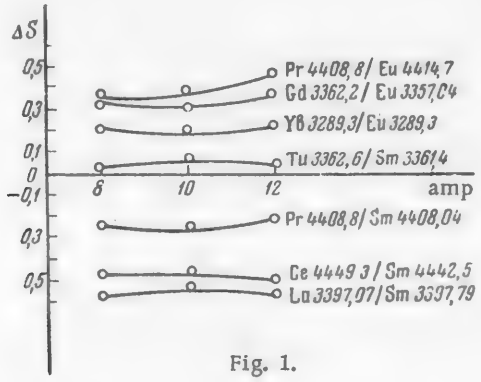

Fig. 1.

Apparatus and excitation conditions. The work was carried out on a DFS-3 diffraction spectrograph with a dispersion of 2 A/mm throughout the whole range. The spectra were excited in an ac arc with a current of 10 amp. The very close similarity in the behavior of many of the rare earths during excitation in the arc ensures a high degree of internal standardization of random variations during excitation in an ac arc.

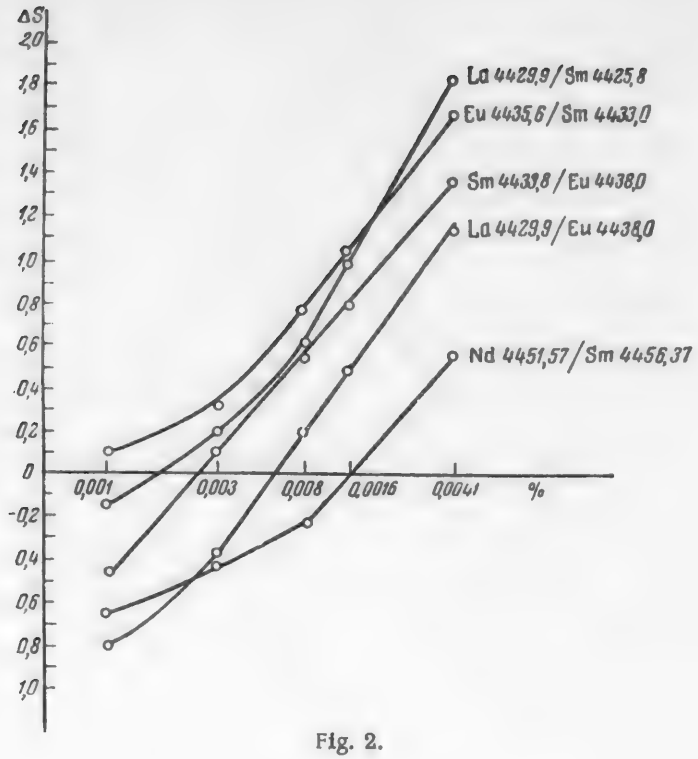
ΔS
2,0
1,8
1,6
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0
-0,2
0,4
0,6
0,8
1,0
0,001
0,003
0,008
0,0016
0,0041
%
La 4429,9 / Sm 4425,8
Eu 4435,6 / Sm 4433,0
Sm 4439,8 / Eu 4438,0
La 4429,9 / Eu 4438,0
Nd 4451,57 / Sm 4456,37

Fig. 2.

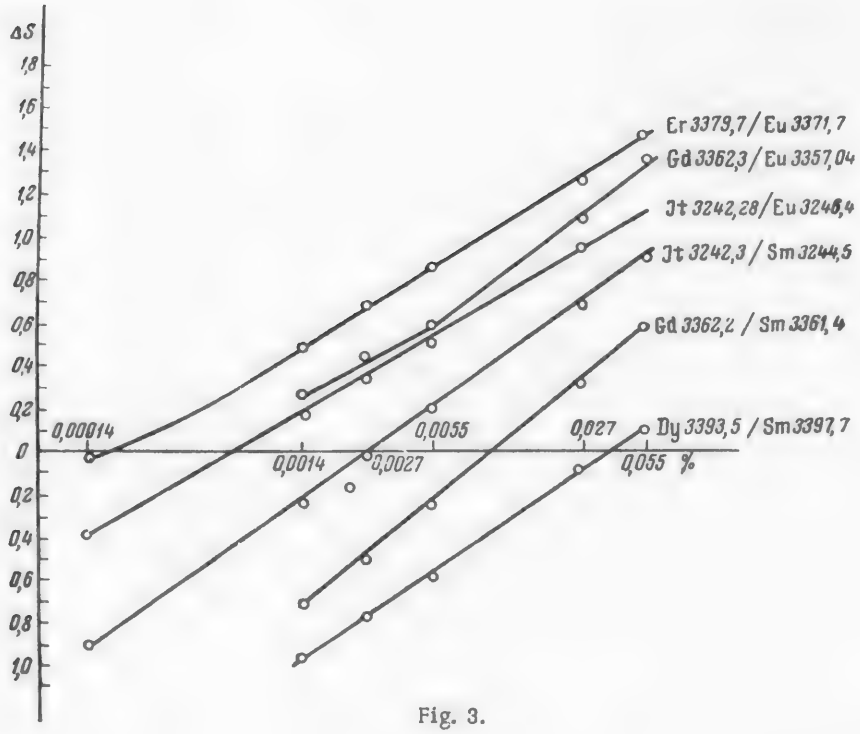
ΔS
1,8
1,6
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0
0,2
0,4
0,6
0,8
1,0
0,00014
0,0014
0,0027
0,0055
0,027
0,055 %
Er 3379,7 / Eu 3371,7
Gd 3362,3 / Eu 3357,04
Jt 3242,28 / Eu 3246,4
Jt 3242,3 / Sm 3244,5
Gd 3362,2 / Sm 3361,4
Dy 3393,5 / Sm 3397,7

Fig. 3.

Main element	Element determined	Analytical lines	Concentration determined %
Samarium	Lanthanum	La 4429,9/Sm 4425,8	0,01 —4,0
	Cerium	Ce 4449,34/Sm 4442,58	0,03 —4,0
	Praseodymium	Pr 4408,84/Sm 4408,04	0,03 —4,0
	Neodymium	Nd 4451,57/Sm 4446,37	0,03 —4,0
	Europium	Eu 4435,6/Sm 4433,0	0,00 8—5,0
	Gadolinium	Gd 3362,24/Sm 3361,44	0,01 —5,0
	Terbium	Tb 3324,4 Sm 3322,7	0,01 —5,0
	Dysprosium	Dy 3393,58 Sm 3397,79	0,01 —5,0
	Holmium	Ho 3398,98 Sm 3397,79	0,008 —5,0
	Erbium	Er 3372,75 Sm 3372,32	0,002 —5,0
	Ytterbium	Yb 3289,37/Sm 3286,57	0,0002—5,0
	Thullium	Tu 3362,61/Sm 3361,64	0,002 —5,0
	Lutecium	Lu 3397,09 Sm 3397,79	0,01 —5,0
	Yttrium	Y 3242,28/Sm 3244,48	0,001 —5,0
Europium	Lanthanum	La 4429,9/Eu 4438,0	0,1 —4,0
	Cerium	Ce 4449,34 Eu 4446,47	0,3 —4,0
	Praseodymium	Pr 4408,84/Eu 4414,76	0,3 —4,0
	Neodymium	Nd 4451,57 Eu 4446,47	0,3 —4,0
	Samarium	Sm 4433,8 Eu 4438,0	0,01 —4,0
	Gadolinium	Gd 3362,24/Eu 3357,04	0,01 —5,0
	Terbium	Tb 3324,4 Eu 3327,04	0,01 —5,0
	Dysprosium	Dy 3393,58 Eu 3394,03	0,01 —5,0
	Holmium	Ho 3398,98 Eu 3394,03	0,008 —5,0
	Erbium	Er 3379,75 Eu 3371,75	0,002 - 5,0
	Ytterbium	Yb 3289,37 Eu 3288,57	0,0002—5,0
	Thullium	Tu 3362,61 Eu 3357,04	0,002 —5,0
	Lutecium	Lu 3397,07 Eu 3394,03	0,01 —5,0
	Yttrium	Y 3242,28/Eu 3246,44	0,001 —5,0

The internal standard chosen was the rare earth forming the bulk of the test material, since this would make compensation of variations in the excitation conditions even more effective.

The wavelength region used for determination of the cerium group was 4400 A, while for determination of elements of the yttrium group the wavelength region used was 3300-3400 A.

Photographic plates type III with a sensitivity of 4.5 GOST units were used. The developer was Chibisova No. 1.

Preparation of standards. The purest oxides of the rare earths available in the laboratory were used for preparing the standards, after the oxides had been calcined at 900°. Two series of standards were prepared by dissolving the corresponding oxides in HCl.

The first series was a mixture of the elements of the cerium group including europium; the concentrations used were as follows: 0.085, 0.033, 0.0085, 0.0066, 0.0022% La, Ce, Pr, Nd, Sm, Eu.

The second series was a mixture of the elements of the yttrium group including yttrium; the concentrations were as follows: 0.111, 0.055, 0.011, 0.0055, 0.0027, 0.00027; Gd, Dy, Tb, Ho, Er, Tu, Lu, Yb, Y.

Since the internal standard used is the rare earth which forms the bulk of the test material (in our case, samarium and europium), the content of this element should be the same both in test samples and in standards. Accordingly, the series of standards indicated were mixed in the proportion of 1 : 1 (by volume) with a 2% solution of the oxide of samarium oxide during analysis of samarium concentrates, and with a 2% solution of europium oxide during the analysis of europium concentrates.

Preparation of samples. The test samples were dissolved to give solutions with concentrations of 1-10% with respect to samarium and europium.

As tests showed, the optimum concentration is 1-5%. When high concentrations are used, a friable deposit is obtained after evaporation of a drop of the solution; this deposit does not stick very well on the electrode end.

Experiments also showed that the optimum concentration of the salts during dissolution of the test sample is 1%. The standards can be prepared beforehand and stored in test tubes closed with ground-glass stoppers.

Choice of analytical lines. The spectra of the rare earths are extremely complex; accordingly, the most difficult problem in the whole analysis is the choice of the analytical lines.

The analytical pairs of lines chosen were those whose components react in the same way to changes in current strength, interelectrode distance, etc.

The relation between the relative blackenings of the line and the current is shown in Fig. 1.

The analytical lines chosen are given in the table.

The three-standards method was used. Calibration curves were constructed within the coordinates ΔS, $\log C$. Some calibration curves are shown in Figs. 2 and 3.

The correctness of the results was evaluated by introducing known amounts of the test elements, and by comparing the results obtained with the results of x-ray spectrographic analysis, when the content of the impurities did not exceed the sensitivity limit of the x-ray spectrographic method. The agreement between the results obtained by the two methods was fully satisfactory. The error of a single determination was ±3-5% relative.

SUMMARY

A technique has been developed for the quantitative determination of rare earths present as impurities in pure samarium and europium oxides. Determinations can be carried out within the concentration limits 0.01-4%; 0.002-5%. The mean error is 3-5% relative. The minimum amount of test sample required for an analysis is 5-10 mg.

LITERATURE CITED

[1] V.A. Tassel and H.A. Wilhelm, J. Opt. Soc. America 38, 518 (1948).

[2] V.A. Tassel and H.D. Cook, Spectrochim Acta 5, 201 (1952).

[3] Kryuger and Shvangiradze, Zhur. Anal. Khim. 9, 11 (1954).*

[4] Kh.I. Zil'bershtein, Zhur. Tekh. Fiz. 25 (1955).

[5] A.N. Zaidel', Tables of Spectral Lines [in Russian] (Gostekhizdat, Moscow-Leningrad, 1952).

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*See C.B. translation.

PHOTOMETRIC DETERMINATION OF GERMANIUM BY MEANS OF o-DIHYDROXYCHROMENOLS

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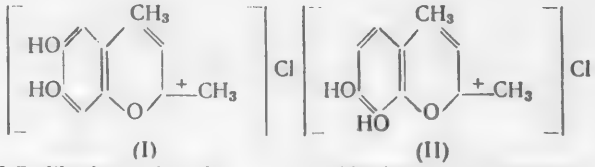
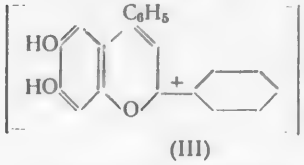
Methods in which colored compounds with organic reagents such as hematin [3], o-dihydroxyazo dyes [4], and phenylfluorone [5] have been used in recent years for the photometric determination of germanium instead of methods based on the formation of germaniomolybdic acid [1] and on its reduction [2]. We have found that benzopyryl or flavyl dyes (chromenols) containing two hydroxy groups in the ortho position in the benzene ring are sensitive reagents for a number of elements, including germanium. It was interesting to find out to what extent these reagents can be used for the photometric determination of germanium. For this purpose, we prepared and studied the following four dihydroxychromenols:

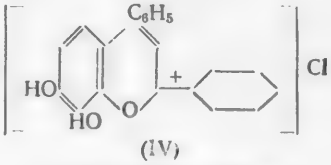


(I) 6,7-dihydroxy-2,4-dimethylbenzopyrylium chloride

(II) 7,8-dihydroxy-2,4-dimethylbenzopyrylium chloride



(III) 6,7-dihydroxy-2,4-diphenylbenzopyrylium chloride



(IV) 7,8-dihydroxy-2,4-diphenylbenzopyrylium chloride

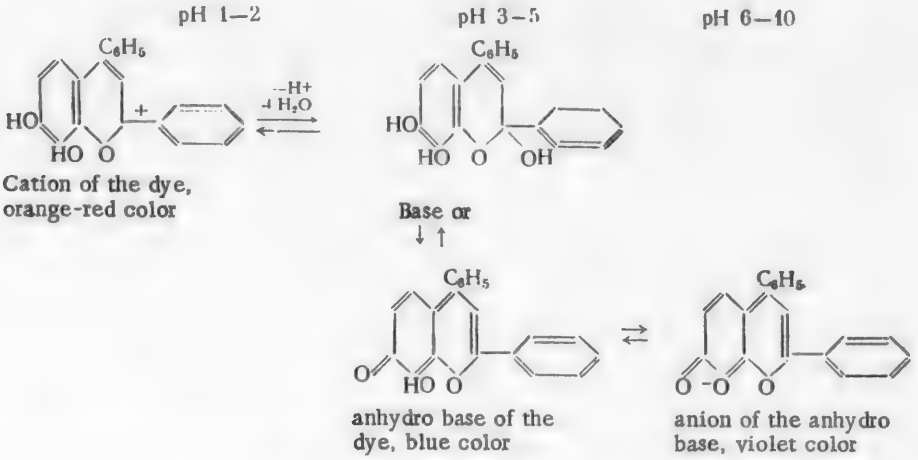
TABLE 1

Colors of Solutions Containing Chromenols as a Function of the pH of the Media

Reagent	Color of the solution at pH									
	1	II	3	4	5	6	7	8	9	10
I	Pale-yellow	← Lemon yellow →					← Bright-yellow →			
II	Lemon-yellow	← Dark-red →				← Brown-red →				
III	Lemon-yellow	← Red-orange →					← Dark-red →			
IV	Orange-red →	← Blue →				← Violet →				

The chlorides of the dihydroxychromenols are crystalline materials which are yellow, red, or dark brown in color. The salts of the dimethyl derivatives are soluble in water, while the salts of the diphenyl derivatives are insoluble in water, but soluble in alcohol to form brightly colored solutions. The colors of aqueous and aqueous-alcohol solutions change with pH (Table 1).

As is evident from Table 1, the dihydroxychromenols are acid-base indicators, which give three colored forms depending on the pH of the solution. Such behavior on their part can be explained by successive ionization, for example, as follows, in the case of 7,7-dihydroxy-2,4-diphenylbenzopyrylium:



Solutions of germanium salts in acid media (0.1 N HCl) give more or less sharp color changes with the reagents (Table 2). A number of other metals behave similarly; they include: zirconium, hafnium, titanium, thorium, molybdenum, tungsten, vanadium, tantalum, niobium, and tin.

TABLE 2

Changes in the Color of Acid Solutions of the Dyes on Addition of Germanium

Reagent	Color of the solution in 0.1 N HCl	Color with addition of germanium
I	Pale yellow	Bright yellow
II	Orange	Red
III	Yellow	Orange-red
IV	Orange	Dark

The colored germanium complexes of the dimethyl derivatives of the chromenols are soluble in water, while those of the diphenyl derivatives are insoluble and separate out as precipitates; they can, however, be kept in solution by using a protective colloid. In Figs. 1-2 are shown the absorption curves for solutions of the reagents (curves 1 and 3) and of solutions of their compounds with germanium (curves 2 and 4). As is evident from these curves, during complex formation with germanium, there is observed a bathochromic shift of the absorption bands of the dye and an expansion of these bands.

Conditions for the photometric determination of germanium in solution by means of dihydroxychromenols. Each of the reagents synthesized was examined with the object of establishing the optimum wavelength at which germanium should be determined, the effect of hydrochloric acid concentration on the optical density of the solution, the stability of the color with time, the optimum amounts of reagent and protective colloid (gelatin), the sensitivity of the method, the germanium concentration range for which the determination can be carried out, and whether or not Beer's law is obeyed.

As the results in Table 3 show, the reagent which proved to be most sensitive and gave the most contrasting color change was 6,7-dihydroxy-2,4-diphenylbenzopyranol. The optical density can be measured both on

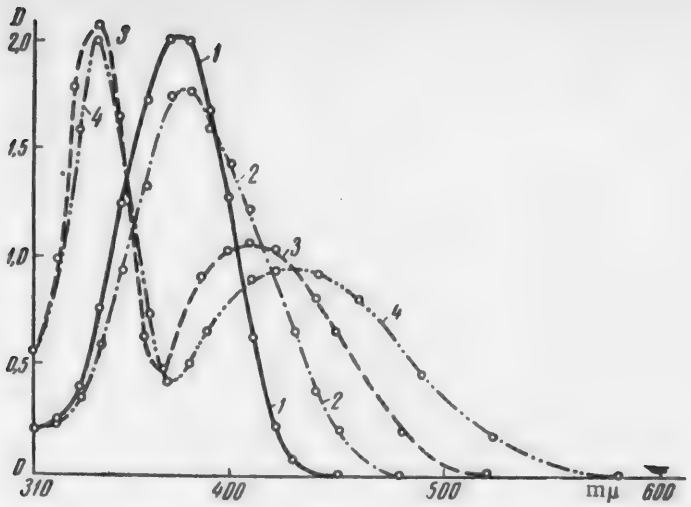


Fig. 1. Absorption curves for solutions of 6,7-dihydroxydimethylbenzopyrylium chloride (1), and of its compound with germanium (2); absorption curves for solutions of 7,8-dihydroxy-2,4-dimethylbenzopyrylium chloride (3), and of its compound with germanium (4).

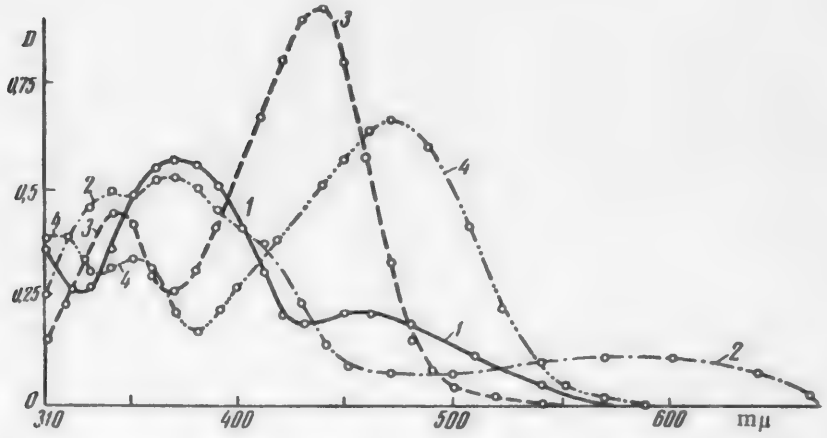


Fig. 2. Absorption curves for solutions of 7,8-dihydroxy-2,4-diphenylbenzopyrylium chloride (1), and of its compound with germanium (2); absorption curves for solutions of 6,7-dihydroxy-2,4-diphenylbenzopyrylium chloride (3), and of its compound with germanium (4).

the SF-4 spectrophotometer, and on the FM-1 photometer or the FÉK-M photoelectrocolorimeter, using a cuvette with a layer thickness of 5 mm (the 6,7-dihydroxyphenyl derivative) and 10 mm (the other reagents).

The color develops immediately on addition of reagents I and II, and reaches a maximum in 3-5 minutes in the case of reagents III and IV; the color subsequently remains constant for 24 hours.

Composition and formation constants of the colored germanium complexes. The composition of the compounds formed between germanium and the tested dihydroxychromenols was studied in each case by the isomolar series method of Ostromyslenskii-Job, by determining the optical density of the solutions at the wavelengths given in Table 3. The experimental conditions used are given in Table 4.

The results obtained (Fig. 3) show that germanium forms compounds with all the reagents in which there are two molecules of reagent for one atom of germanium.

TABLE 3

Conditions for Determination of Germanium by the Dihydroxychromenols Studied

Reagent	Wavelength at which optical density is measured, mμ	Optimum HCl concentration, N	Amount added per 10 ml solution		Sensitivity of the method, γ (in 10 ml of solution)	Maximum amount Ge (γ) in 10 ml solution at which Beer's law is obeyed
			reagent	1% gelatin solution		
I	420	0.1 —0,6	2 ml of 0.2% aqueous solution	—	1	100
II	500—530	0.05—0,2	0.5 ml of 1% aqueous solution	—	2	100
III	500	0.1 —0,6	0.5 ml of 0.2% alcoholic solution	0,5 ml	0.1	25
IV	600—630	0.05—0,2	0.5 ml of 0.2% alcoholic solution	0,5 ml	1	40

TABLE 4

Conditions Used for the Determination of the Composition of the Colored Compounds Formed Between Germanium and the Dihydroxychromenols

Reagent	Total concentration of components, M	Acidity of the solution with respect to HCl, N	Alcohol concentration, %	Gelatin concentration, %
I	$2 \cdot 10^{-2}$	0.5	—	—
II	$2 \cdot 10^{-2}$	0.1	—	—
III	$2 \cdot 10^{-3}$	0.1	1.0	0.04
IV	$2.5 \cdot 10^{-3}$	0.2	1.0	0.04

The apparent formation constants of the water-soluble, colored complexes, formed between germanium and the dimethyl derivatives of the chromenols in 0.1-0.2 N HCl, according to the equation $GeO_2 + 2HA \rightleftharpoons GeOA_2 + H_2O$, were determined by measuring the optical density of a series of solutions containing the components in stoichiometric proportion, and in solutions where the concentration of reagent was in excess, so that dissociation of the complexes was suppressed. The colored colloidal solutions of the complexes formed with the diphenyl derivatives in the presence of gelatin also conform to the law of mass action in a certain concentration range, and the equations for the formation of the colored soluble complexes are applicable to them. This follows from the fact that on determining the composition of these complexes on the basis of the slope of the logarithmic curves, correct results are obtained on using the equation

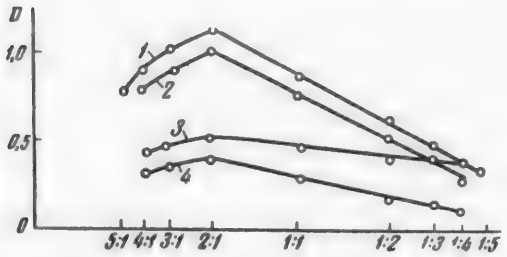


Fig. 3. Composition of the colored compounds formed between germanium and the dihydroxychloromenols: 1) 7,8-dihydroxy-2,4-dimethylbenzopyrylium chloride; 2) 7,8-dihydroxy-2,4-diphenylbenzopyrylium; 3) 6,7-dihydroxy-2,4-dimethylbenzopyrylium chloride; 4) 6,7dihydroxy-2,4-diphenylbenzopyrylium.

$$\frac{[GeO^{2+}][A^-]^n}{[GeOA_2]} = K'_{\text{dissoc.}}$$

and not the equation

$$[GeO^{2+}][A^-]^n = L_{\text{sol.}}$$

Transforming these equations, and replacing the concentrations of the ions by the concentrations of the components which are proportional to them, we get from the first equation:

$$n \lg [HA] = \lg \frac{[GeOA_2]}{[GeO_2]} + \text{const},$$

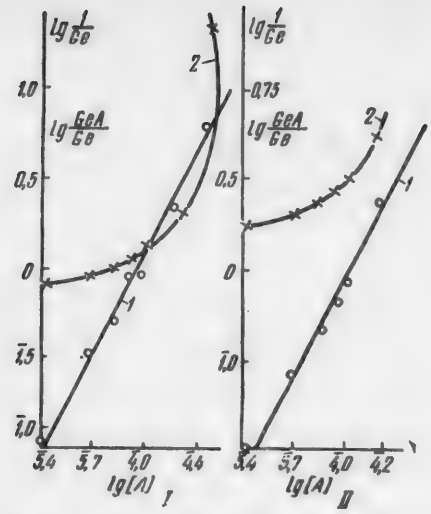


Fig. 4. Composition of the complexes by the method of the slope of the logarithmic curves calculated on the basis of the equations

$$\lg \frac{[GeOA_2]}{[GeO_2]} = n \lg [HA] — (1)$$

for the solutions and

$$\lg \frac{1}{[GeO_2]} = n \lg [A^-] — (2)$$

for formation of precipitates I with 6,7-dihydroxy-2,4-diphenylbenzopyrylium; II with 7,8-dihydroxy-2,4-diphenylbenzopyrylium.

while from the second, we get:

$$n \lg [A^-] = \lg \frac{1}{[GeO_2]} + \text{const.}$$

As is evident from Fig. 4, the values for $\log[GeOA_2]/[GeO_2]$, calculated on the basis of the first equation for the soluble complexes, lie on a straight line with $\tan\alpha = 2$, while the values of $\log 1/[GeO_2]$, calculated on the basis of the second equation, lie on a curve. Accordingly, it is possible to calculate the apparent formation constants of the complexes with the diphenyl derivatives of the chromenols.

Calculations were made by means of the formula

$$K'_{\text{formation}} = \frac{(1-\alpha)}{4\alpha^3 C^3} = \frac{1}{K'_{\text{dissoc.}}}$$

where α is the percentage dissociation of the complex for stoichiometric concentrations of the components, and C is the concentration of germanium ions in solution. The degree of dissociation α was calculated by means of the formula $\alpha = (E_{max} - E_{stoich})/E_{max}$, in which E_{max} and E_{stoich} are the optical densities of the solutions when excess reagent and stoichiometric proportions of the concentrations are used, respectively. The experimental conditions and the results obtained are given in Table 5.

The highest formation constant was found for the 6,7-dihydroxy-2,4-diphenyl derivative.

Masking of foreign metals in the reaction with the chromenols. A number of masking agents were tested for simplifying the analytical procedure in the presence of not very large amounts of foreign elements. The most suitable masking agent proved to be a mixture of sodium ethylenediaminetetracetate, hydrogen peroxide, and phosphoric acid. Sodium ethylenediaminetetracetate masks zirconium, hafnium, thorium, iron (III), tin (IV), and bismuth; phosphoric acid masks titanium, while hydrogen peroxide decreases the effect of molybdenum, tungsten, antimony, and vanadium. In the presence of the amounts of the masking agents indicated below, the following amounts of the listed elements can be present in 25 ml of solution: up to 12.5 mg bismuth, 2.5 mg thorium, 1.5 mg iron (III), 1.0 mg titanium, 0.75 mg aluminum, 0.5 mg zirconium, or 1 mg hafnium, 0.4 mg tin (IV), 100 γ vanadium, 40 γ niobium, 30 γ tantalum, 20 γ tin (IV), 15 γ tungsten, 5 γ molybdenum, and 5 γ antimony. The intensity of the color of the germanium complex does not alter appreciably under these conditions. These masking agents can also be used for the determination of germanium by means of phenylfluorone and other similar reagents.

Experimental procedure. a) In the presence of small amounts of foreign elements, without preliminary separation. A known amount of test solution is pipetted into a 25 ml standard flask, and 1 ml of 5 N HCl, 0.2 to 0.3 ml of phosphoric acid (1 : 1), 2-3 drops of hydrogen peroxide, and 2 ml of a 5% solution of sodium ethylenediaminetetracetate added in succession with stirring; 1 ml of a 1% solution of gelatin and 1.25 ml of a 0.2% ethanolic solution of the reagent (6,7-dihydroxy-2,4-diphenylbenzopyranol) are then added. The final solution is diluted with distilled water to the mark, and after three minutes the optical density is measured relative to the solution from the control test on a SF-4 spectrophotometer in 20 mm cuvettes at 500 mμ. The germanium content is determined by means of a calibration curve. The calibration curve is linear up to concentrations of 25 γ of germanium in solution (Fig. 5).

Table 6 contains the results of determination of germanium in synthetic mixtures.

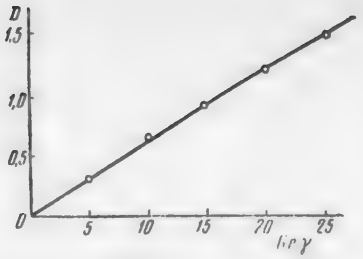
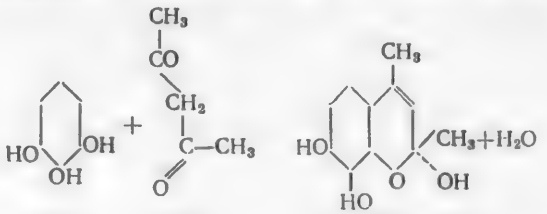


Fig. 5. Calibration curve for the spectrophotometric determination of germanium by means of 6,7-dihydroxy-2,4-diphenylbenzopyrylinium chloride.

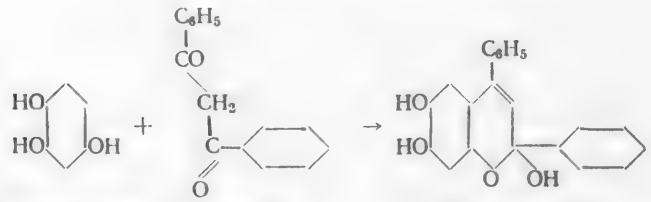
b) After removal from interfering elements by extraction with carbon tetrachloride. Decomposition of the ore sample and separation of germanium are carried out as in the work of Nazarenko et al [5]. The solution of $GeCl_4$ in carbon tetrachloride obtained during the analytical process is extracted three times with water, 4-ml portions of water being used each time. The aqueous solution is filtered through a small filter in order to remove drops of carbon tetrachloride, the filter is washed with a small amount of water, and to the combined filtrate and wash liquors are added 1 ml of 5 N hydrochloric acid, 1 ml of 1% gelatin solution, 1.25 ml of a 0.2% ethanolic solution of the reagent, and the whole diluted to 25 ml with water in a standard flask. The optical density is measured after three minutes.

Table 7 contains the results obtained during the determination of germanium in silicate rocks and sulfide ores. The method gives satisfactory results.

Synthesis of the dihydroxychromenols [6]. The dihydroxychromenols used in the work described here are readily prepared by the condensation of 1,3-diketones with trifunctional phenols:



pyrogallol — acetylacetone — 7,8-dihydroxy-2,4-dimethylbenzopyranol



hydroxyhydroquinone — dibenzoylmethane — 6,7-dihydroxy-2,4-diphenylbenzopyranol

As an example, we shall describe the synthesis of 6,7-dihydroxy-2,4-diphenylbenzopyranol [7].

TABLE 5

Experimental Conditions and Results of the Determination of the Apparent Formation Constants and Molar Extinction Coefficients of the Germanium Complexes with Dihydroxychromenols

Reagent	Ge concentration, M	HCl concentration, N	Thickness of layer in cuvette, mm	Values found		▪		Molar extinction coefficient
				$E_{stoich.}$	E_{max}			
I	$2 \cdot 10^{-4}$	0,1	10	0,51	1,1	0,536	$1,9 \cdot 10^{7}$	5 500
	$1,6 \cdot 10^{-3}$	0,1	10	0,56	0,75	0,252	$0,5 \cdot 10^{7}$	4 700
II	$2 \cdot 10^{-4}$	0,1	10	0,075	0,585	0,87	$1,3 \cdot 10^{7}$	2 925
III	$1 \cdot 10^{-4}$	0,1	5	0,74	1,1	0,326	$4,8 \cdot 10^{8}$	25 000
IV	$1 \cdot 10^{-4}$	0,2	5	0,275	0,78	0,52	$0,8 \cdot 10^{8}$	15 600

TABLE 6

Determination of Germanium in Mixtures of Cations Without Preliminary Separation

Ge taken, γ	Added														Ge found, γ	Difference, γ
	Fe(III), mg	Al, mg	Bi, mg	Ti, mg	Hf, mg	Zr, mg	Th, mg	Ta, γ	Nb, γ	Sb(III), γ	V, γ	Mo, γ	Sn(IV), γ	W, γ		
1	1	0,5	5	0,5	—	—	—	20	—	—	—	5	—	—	1	0,0
2,5	1	0,75	—	—	—	0,2	1	—	—	—	—	—	—	—	3	+0,5
2,5	—	—	—	—	—	—	—	20	—	—	50	5	—	10	2,4	—0,1
5	1	0,5	5	—	1	—	—	20	20	4	—	—	—	—	5,6	+0,6
5	1	0,5	2	—	—	—	1	—	—	—	—	—	15	—	5,0	0,0
10	1	0,75	—	—	—	0,25	1	—	—	—	—	—	—	—	10,4	+0,4
10	—	—	—	—	—	—	—	20	—	—	50	5	—	10	10,3	+0,3
12	1	0,5	—	0,2	—	—	—	20	—	—	50	5	—	—	12,6	+0,6
18	1,5	0,75	—	0,5	—	—	1	—	—	4	—	—	—	15	17,9	—0,1
20	1	0,5	5	0,2	—	—	—	20	—	4	70	5	—	—	20	0,0

TABLE 7

Determination of Germanium in Rocks and Ores

Test material	Ge added, %	Ge found, together with added germanium%	Difference, %
Silicate rock (sample No. 1)	—	0,00058	
	0,0005	0,00105	—0,00003
Silicate rock (sample No. 2)	—	0,00038	
	0,001	0,00136	—0,00002
Silicate rock (sample No. 3)	—	0,00095	
	0,0007	0,00161	—0,00004
Sulfide-zinc ore (sample No. 1)	—	0,00029	
	0,0008	0,00109	0,000
Sulfide-zinc ore (sample No. 2)	—	0,00078	
	0,0005	0,00128	0,000
Pyrites	0,001	0,00012	
		0,0011	—0,00002

0.6 g of pyrogallol A (triacetylhydroxyhydroquinone) is dissolved in 4 ml of glacial acetic acid and a stream of dry hydrogen chloride passed through the solution for half an hour; 0.6 g of dibenzoylmethane is added and hydrogen chloride passed through for a further 4-5 hours. The flask is then tightly sealed and allowed to stand for 24 hours. A crystalline, yellow-orange precipitate separates out. The mixture is cooled in ice for an hour and the preparation which separates out is filtered off and washed with ether. In order to purify the product, a saturated solution of it is prepared in alcohol by heating, the solution is filtered and an equal volume of concentrated hydrochloric acid is added. The chromenol chloride which separates out on cooling and on rubbing with a rod is filtered off, and washed with a 1% solution of hydrochloric acid; it is finally dried in air.

SUMMARY

A study has been made of the behavior of germanium toward four representatives of the group of o-dihydroxybenzopiperyl dyes (dihydroxy chromenols). 6,7-Dihydroxy-2,4-diphenylbenzopiperylium chloride gives the most sensitive reaction; in acid media (0.1 N HCl) the color changes from yellow to orange-red. This reagent permits determination of 0.1-25 γ of germanium in 10 ml of solution. A technique has been developed for the determination of germanium in various materials. It has been established that the ratio between the number of molecules of reagent and the number of atoms of germanium in the colored complexes formed is 2:1; the apparent formation constants of the complexes have been determined.

LITERATURE CITED

[1] L.P. Alimarin and B.N. Ivanov-Émin, Zhur. Priklad. Khim. 9, 1334 (1936).

[2] N.S. Poluéktov, Zavodskaya Lab. 5, 27 (1936).

[3] H. Newcombe, W.A.E. McBryde, J. Barlett, and F.E. Beamish, Analyt. Chem. 23, 1023 (1951

[4] P. Bevillard, Bull. Soc. Chim. France N 3, 307 (1954).

[5] V.A. Nazarenko, N.V. Lebedeva, and R.V. Ravitskaya, Zavodskaya Lab. 24, 9 (1958).•

[6] "Heterocyclic Compounds," Collection edited by R. Elderfield [Russian translation] (IL, Moscow, 1954) vol. 2, p. 214.

[7] C. Bülow and W. Sicherer, Ber. 34, 3916 (1901).

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•See English translation.

COMPLEXONOMETRIC DETERMINATION OF ZIRCONIUM

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Methods for the complexonometric determination of zirconium are based on direct titration of zirconium with sodium ethylenediaminetetracetate (EDTA-Na) in the presence of the appropriate metal indicator [1-6], and on the back titration of excess EDTA-Na with some salt [7-13]. The most interesting method for the direct titration of zirconium with EDTA-Na is the method using p-nitrobenzeneazopyrocatechol as indicator, first suggested by N.S. Poluéktov et al [5]. Titration is carried out in a medium of 2 N HCl which determines the high selectivity of the method, since under these conditions all the other metals (with the exception of Hf) do not react with EDTA. The drawback of this method, which is also inherent in other methods based on direct titration of zirconium, is the indistinct change in the color at the equivalence point. This apparently is determined not so much by the properties of the indicators used, but by the very process of complex formation between zirconium and EDTA-Na.

Titration of zirconium with EDTA-Na is usually carried out in a hot solution, while it is often recommended that the solution be boiled again near the equivalence point and up to the end of the titration. But, under these conditions, the reaction does not go to completion, and a direct proportionality between the amount of EDTA-Na solution used for titration and the amount of zirconium is not observed. When the theoretical amount of EDTA-Na with respect to zirconium is used (1 ml of 0.1 EDTA-Na is equivalent to 9.122 mg Zr) the results are usually 4-5% (relative) low [6]. Accordingly, in practical work, an empirical titer is used for zirconium, which is established by titrating a known amount of zirconium with EDTA-Na.

Direct-titration methods give satisfactory results when zirconium is determined in comparatively pure solutions; for example, in solutions of zirconium sulfate and oxychloride free from large amounts of other elements. Extension of these methods to more complex mixtures obtained during the analysis of ores, concentrates, cakes, and other products often does not yield satisfactory results; this led us to use the back-titration method.

When the back-titration technique is used, more consistent results can be obtained by boiling the solution of the zirconium salt with EDTA-Na, taken in excess, in a medium of 2 N HCl. Under such conditions, the interaction of zirconium with EDTA-Na proceeds to completion; in this way, the basic cause for the error in direct titration is eliminated. Existing methods of back titration did not satisfy us for a variety of reasons. Back titration with bismuth nitrate [12] is inconvenient for mass determinations, since, in order to obtain reproducible results, the pH of the medium must be accurately maintained (pH 2). This is only possible by using a pH-meter, while for amperometric determination of the equivalence point [13] a polarographic setup is required.

Back titration of excess EDTA-Na with a ferric salt using salicylic, sulfosalicylic acids [9-11], or potassium benzohydroxamate [7, 8] as indicators is widely used abroad. But, since the titration is carried out at pH 4-6, where many other elements also form stable complexonates, such elements have to be removed beforehand.

Moreover, the drawback of the direct-titration method is also inherent in these methods; namely, as a rule, the introduction of EDTA-Na into the test zirconium solution is carried out at room temperature while the pH of the medium is usually not less than 1. Accordingly, here again, interaction of zirconium with EDTA-Na is not complete, this being the main source of error during the determination. Taking all these facts into account, we decided to concentrate on that variant of the back-titration method which ensures that the reaction with EDTA-Na proceeds to completion. For this purpose, the EDTA-Na is introduced into a boiling solution of zirconium (2 N HCl), and the solution boiled for a few more minutes. Under these conditions, the zirconium is selectively and completely bound as its complexonate. Excess EDTA-Na is titrated with a solution of thorium nitrate.

Thus, determination of zirconium in various materials consists of the following stages: an aliquot of test material is brought into solution by fusing it with potassium bifluoride, with subsequent treatment of the melt with sulfuric acid; zirconium hydroxide is precipitated from the sulfuric acid solution with ammonia, and is dissolved in hot 2 N HCl. To the boiling hydrochloric acid solution of zirconium is added a measured excess of a standard EDTA-Na solution; the solution is boiled for several minutes and then cooled to room temperature; it is neutralized to pH 2.3-2.5, and excess EDTA-Na titrated with a solution of thorium nitrate using arsenazo, also called uranon* [14, 15], as indicator. The optimum amounts of zirconium for a determination are 5-80 mg. The effect of foreign elements on zirconium determination can be seen from the results given in Table 1.

TABLE 1

Effect of Foreign Elements on the Complexonometric Determination of Zirconium (15.37 mg Zr was used in the first 15 experiments, and 15.59 mg Zr in the remainder)

Impurity introduced, mg	Zr found, mg	Error, %		Impurity introduced mg	Zr found, mg	Error, %	
		abs.	rel.			abs.	rel.
30 Zn^{2+}	15,37	0,0	0,0	50 UO_2^{2+}	15,37	0,0	0,0
500 Zn^{2+}	15,37*	0,0	0,0	500 WO_4^{2-}	15,37*	0,0	0,0
500 Zn^{2+}	15,37**	0,0	0,0	500 MoO_4^{2-}	15,28*	—0,09	—0,6
200 Cu^{2+}	15,46	+0,09	+0,6	200 VO_3^-	15,46*	+0,09	+0,6
500 Cu^{2+}	15,37**	0,0	0,0	5 Fe^{3+}	15,59	0,0	0,0
5 Ni^{2+}	15,28	—0,09	—0,6	3 Ti^{IV}	15,59	0,0	0,0
200 Ni^{2+}	15,46**	+0,09	+0,6	15 Ti^{IV}	15,69***	+0,1	+0,6
15 Co^{2+}	15,37	0,0	0,0	100 Ce^{3+}	15,69	+0,1	+0,6
200 Co^{2+}	15,41**	+0,04	+0,25	200 La^{3+}	15,69	+0,1	+0,6
500 Al^{3+}	15,41*	+0,04	+0,25	200 Nd^{3+}	15,69	0,0	0,0
150 Mn^{2+}	15,37	0,0	0,0				

Note. After precipitation of zirconium with sodium hydroxide (*), ammonia (**), and ammonia in the presence of hydrogen peroxide (***).

TABLE 2

Complexonometric and Gravimetric Phosphate Determinations of Zirconium

Test material	Zr found by complexonometric method	Mean value of Zr, %	Zr found by phosphate method, % (mean of three determinations)	Deviation, abs., %
Ore concentrate	38,47; 38,49; 38,76	38,57	38,62	—0,05
Cake	12,17; 12,29; 12,17; 12,17	12,20	12,29	—0,09
»	17,16; 17,28; 17,32	17,25	17,10	+0,15
»	4,26; 4,26; 4,26	4,26	4,28	—0,02
»	18,20; 18,02; 18,02	18,08	18,21	—0,13
»	10,47; 10,47; 10,47	10,47	10,36	+0,11
»	2,68; 2,68; 2,68	2,68	2,67	+0,01
»	2,80; 2,68; 2,68	2,72	2,76	—0,04
	13,03; 13,03	13,03	12,96	+0,07
	7,07; 7,07	7,07	7,18	—0,11
	1,83; 1,83; 1,85	1,84	1,85	—0,01

Th^{4+}, Bi^{3+}, PO_4^{3-}, F^-, and the anions of oxalic, tartaric, citric, and other acids interfere with the determination in all cases.

Comparison of the results obtained by the titrimetric method and by a gravimetric phosphate method indicates that good agreement is obtained between them (Table 2).

*Xylenol orange can also be used as an indicator.

Analytical procedure. 0.1-0.2 g of test material, depending on the expected zirconium content, is fused in a platinum basin with 1-3 g of potassium bifluoride in a muffle until a transparent melt is obtained. On cooling, 15-20 ml of concentrated H_2SO_4 is added to the melt, and the mixture evaporated on a sand bath until copious sulfuric acid fumes are evolved.

On cooling, the sulfuric acid solution is transferred from the basin into a 300 ml beaker, and, depending on the composition of the test material, zirconium is separated by one of the known methods.

a) Determination of Zirconium in the Presence of Zn^{2+}, Al^{3+}, Fe^{3+}, Sn^{2+}, Sn^{4+}, VO_3^-, Cr_4^{2-}, MoO_4^{2-}, WO_4^{2-}, PO_4^{3-}

To the sulfuric acid solution of zirconium is added, in the cold, a 20% solution of sodium hydroxide until the zirconium hydroxide has been precipitated completely; 5-10 ml of the sodium hydroxide solution is then added in excess. The volume of the solution plus precipitate should not be less than 200 ml. The precipitate is filtered off through not too fine a filter paper (white band) and washed 6-8 times with 5% sodium hydroxide solution. The washed precipitate is washed off the filter paper with a hot 2 N solution of hydrochloric acid into the beaker in which the precipitation was effected and is heated until it dissolves completely (the volume of the solution should not exceed 100 ml). The solution is boiled for 2-3 minutes and ascorbic acid added to reduce Fe^{3+}; 0.05 M EDTA-Na solution is pipetted into the boiling solution. The solution is boiled for 2-3 minutes and then cooled to room temperature, 1-2 drops of a 1% alcoholic solution of α-dinitrophenol is added, and the solution neutralized with ammonia until it has a bright-yellow color; hydrochloric acid (1:2) is then added dropwise, until the color disappears (pH 2.3-2.4). Six to eight drops of a 0.1% aqueous solution of uranon (or 2-3 drops of a 0.5% solution of xylenol orange) is added, and excess EDTA-Na back titrated with a solution of thorium nitrate until the color changes from bright rose to blue-violet.

b) Determination of Zirconium in the Presence of Zn^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+} (T_1^{4+} not more than 15 mg) and in the Absence of PO_4^{3-}

This method can also be used for the analysis of such materials as copper-zirconium ligatures.

To the original sulfuric acid solution is added 1.5-3 ml of 30% H_2O_2 and (in the cold) a 25% ammonia solution, until the zirconium hydroxide has been completely precipitated; 3-5 ml of the ammonia solution is then added in excess (the volume of the solution should not be less than 250 ml). The precipitate is filtered through not too fine a filter paper (white band) and washed 6-8 times with a cold 2% solution of NH_4Cl containing a small amount of ammonia and H_2O_2. The precipitate is washed off the filter with hot 2 N hydrochloric acid into the beaker in which the precipitation was carried out, and the procedure outlined above then followed.

A single determination does not take more than 1-1.5 hours, without taking into account the time taken to decompose the test material.

SUMMARY

A complexonometric method is suggested for the determination of zirconium; it consists of the following stages. The test material (ores, concentrates, cakes, alloys, etc.) is decomposed by a suitable method, and the zirconium is precipitated with ammonia or sodium hydroxide, the precipitate is dissolved in 2 N HCl and is boiled with excess EDTA-Na, the pH of the solution is then adjusted to 2.3-2.4, and excess EDTA-Na is back titrated with thorium nitrate using uranon (arsenazo) or xylenol orange as indicator.

The experimental error does not exceed ±0.6% (relative).

The method has been used for the determination of zirconium in ores, cakes, and concentrates containing from 2 to 40% of zirconium, and gave satisfactory results.

LITERATURE CITED

[1] J. Fritz and M. Fulda, Analyt. Chem. 26, 1206 (1954).

[2] A. Musil and M. Theis, Z. Analyt. Chem. 144, 427 (1955).

[3] G. Banerjee, Z. Analyt. Chem. 147, 105 (1955).

[4] V.G. Goryushina and V.M. Vladimirova, Zavodskaya Lab. 22, 1171 (1956).

[5] N.S. Poluéktov, L.I. Kononenko, and T.A. Surichan, Zavodskaya Lab. 23, 660 (1957).

[6] V.G. Goryushina and E.V. Romanova, Zavodskaya Lab. 23, 781 (1957).

[7] G. Milner and J. Edwards, Analyst 80, 957 (1955).

[8] G. Milner and G. Barnett, Analyt. Chim. Acta 14, 414 (1956).

[9] P. Sweetser and C. Bricker, Analyt. Chem. 26, 195 (1954).

[10] G. Milner and P. Phennah, Analyst 79, 474 (1954).

[11] G. Milner and J. Edwards, Analyt. Chim. Acta 13, 230 (1955).

[12] J. Fritz and M. Johnson, Analyt. Chem. 27, 1653 (1955).

[13] V.M. Vladimirova, Zavodskaya Lab. 22, 5, 529 (1956).

[14] Yu.A. Chernikhov, V.F. Luk'yanov, and A.B. Kozlova, Zhur. Anal. Khim. 14, 567 (1959).*

[15] V.L Kuznetsov, Zhur. Anal. Khim. 7, 226 (1952).*

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THE SOLUBILITY OF ZIRCONIUM CUPFERRONATE

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Cupferron (ammonium nitrosophenylhydroxylamate) finds wide application in the analytical chemistry of zirconium. The first determination of zirconium by means of cupferron was carried out by Schroder [1]. Later, cupferron was used by other authors [2] for removing impurities from zirconium. Cupferron can be used for separating zirconium from Al^{3+}, Mg^{2+}, Be^{2+}, Zn^{2+}, UO_2^{2+} and other elements which are not precipitated by this reagent in an acid medium. That such a separation is possible depends on the completeness of precipitation of zirconium with excess cupferron in the medium selected. Accordingly, a study of the solubility of zirconium cupferronate as compared with the solubility of the cupferronates of the elements which we were interested in is of considerable importance.

Zirconium forms a white, bulky precipitate of $Zr(C_6H_5NNOO)_4$ [1] with cupferron. Precipitation is quantitative even in 4 N sulfuric acid or in 6 N hydrochloric acid. Until recently, no accurate data were available on the solubility of zirconium cupferronate. Pinkus and Martini [3] have studied the solubility of the cupferronates of a series of metals. The method which they developed consisted of shaking the metal cupferronate with water until saturation was reached at a constant temperature; this method, however, could not be used for zirconium cupferronate because of the large tendency of zirconium to hydrolyze. Moreover, values of the solubility of the cupferronates which are not determined under the conditions in which the metals are precipitated and separated by means of cupferron, cannot serve as a criterion for the quantitative precipitation of the cupferronates.

Pyatnitskii [4] suggested a new method for the determination of the solubility of metal cupferronates. The method consists in determining the equilibrium constants of the reaction between the metals and cupferron in an acid medium, i.e., under conditions approximating to those used for precipitation of the metals by cupferron. From the equilibrium constants of the reactions the solubility product (L_S), and hence, the solubility of the metal cupferronate, are determined. In its application to zirconium, Pyatnitskii's method has a number of advantages over other methods; we used it for determining the solubility of zirconium cupferronate.

The equilibrium constant is readily found by means of the following simple equations:

$$Me^{4+} + 4HR \rightleftarrows MeR_4 + 4H^+, \quad (1)$$

$$K_{eq} = [H^+]^4/[Me^{4+}][HR]^4. \quad (2)$$

The solubility product L_S for MeR_4 can be expressed by the formula:

$$L_S = [Me^{4+}][R^-]^4. \quad (3)$$

The dissociation constant of nitrosophenylhydroxylamic acid is equal to

$$K_S = [H^+][R^-]/[HR]. \quad (4)$$

Substituting the value of $[H^+]$ from Eq. (4) in Eq. (2), we get

$$L_S = K_S^4/K_{eq} \quad (5)$$

Equation (5) gives the possibility of calculating the value of the solubility product of the metal cupferronate, as long as the equilibrium constant of the reaction is determined ($K_{eq.reaction}$). The value of the dissociation constant of nitrosophenylhydroxylamine determined by Pyatnitskii, and which proved to be $5.3 \cdot 10^{-5}$, was substituted in the equation.

The method used for determining the solubility consisted of the following. Into a 100-ml beaker placed in a thermostat maintained at 20° was introduced an accurate amount of zirconium in the form of a 1 M sulfuric acid solution, the acidity of the solution was then accurately adjusted with respect to sulfuric acid, taking into account the amount of aqueous cupferron solution added. The ionic strength of the solutions in each case was adjusted to 2 by means of ammonium sulfate. Solubility determinations were carried out in a sulfuric acid medium (not in perchloric acid solutions, which prevent complex formation), because of the fact that, during the analysis of zirconium for impurities, sulfuric acid solutions are obtained in bringing the test material into solution. Zirconium was precipitated by adding, from a buret, a known volume of a freshly prepared standard aqueous solution of cupferron, taken in excess as compared with the stoichiometric amount. The solution and precipitate were stirred for 2-3 minutes, and the precipitate filtered through a No. 4 glass filter. The concentration of the zirconium in the filtrate was determined by the method of labeled atoms, using Zr^{95} (purified from radioactive Nb^{95}) as radioactive indicator.

The γ-activity of the filtrates was measured on a γ-scintillation setup and was expressed in terms of the relative values of the number of impulses per minute with a reproducibility of the order of ±5% (relative). 5 and 10 mg of zirconium were taken for the experiments. $4.115 \cdot 10^5$ impulses/minute corresponded to one milligram of zirconium. However, it was impossible to use the value of the total concentration of zirconium in solution for calculating the equilibrium constant. Zirconium compounds hydrolyze strongly in aqueous solutions. Zirconium forms a considerable number of complex ions, particularly in sulfuric acid media; zirconium also has a tendency to form polymeric compounds. Depending on the hydrogen-ion concentration, in aqueous solutions, the following equilibrium is established:

$$Zr^{4+} + n\,H_2O \rightleftarrows Zr(OH)_n^{4-n} + n\,H^+. \tag{6}$$

consequently, in addition to quadrivalent Zr^{4+} ions, tri-, di-, and uni-charged complex ions will be present in solution, and, accordingly, must be taken into account in calculating the equilibrium constants ($K_{eq.}$) of the reaction.

Connick and McVey [5] in their study of complex formation of zirconium with sulfate ions, adduce the following formation constants for the complexes:

$$Zr^{4+} + HSO_4^- = ZrSO_4^{2+} + H^+;\ K_1 = \frac{[ZrSO_4^{2+}]\,[H^+]}{[Zr^{4+}]\,[HSO_4^-]} = 4{,}6 \cdot 10^1; \tag{7}$$

$$ZrSO_4^{2+} + HSO_4^- = Zr(SO_4)_2 + H^+;\quad K_2 = \frac{[Zr(SO_4)]_2\,[H^+]}{[ZrSO_4^{2+}]\,[HSO_4^-]} = 53; \tag{8}$$

$$Zr(SO_4)_2 + HSO_4^- = Zr(SO_4)_3^{2-} + H^+;\ K_3 = \frac{[Zr(SO_4)_3^{2-}]\,[H^+]}{[Zr(SO_4)_2\,[HSO_4^-]} = 1. \tag{9}$$

Solovkin [6], during a study of the extraction of micro amounts of zirconium by tributylphosphate as a function of hydrogen-ion concentration and nitrate-ion concentration, determined the constants for the successive hydrolysis reactions of Zr^{4+}, and at an ionic strength of the solution of 2 these proved to be

$$Zr^{4+} + H_2O = Zr(OH)^{3+} + H^+;\ K_4 = \frac{[Zr(OH)^{3+}]\,[H^+]}{[Zr^{4+}]} = 0{,}6; \tag{10}$$

$$Zr(OH)^{3+} + H_2O = Zr(OH)_2^{2+} + H^+;\ K_5 = \frac{[Zr(OH)_2^{2+}\,[H^+]}{[Zr(OH)^{3+}]} = 0{,}24; \tag{11}$$

$$Zr(OH)_2^{2+} + H_2O = Zr(OH)_3^{+} + H^+;\ K_6 = \frac{[Zr(OH)_3^{+}]\,[H^+]}{[Zr(OH)_2^{2+}]} = 0{,}09. \tag{12}$$

No quantitative characteristic for the formation of polymeric ions in sulfuric acid solutions is available. Connick and Reas [7] studied the polymerization of zirconium in 1 and 2 M perchloric acid solutions, and showed that polymerization occurs at comparatively high zirconium concentrations (10^{-3} to 10^{-4} mole/liter). At lower concentrations and higher acidity zirconium is found in the form of the quadri-charged monomer. Under the conditions we used in our work, in which the zirconium concentration is less than 10^{-3} mole/liter, polymerization cannot play an important role, and, compared with the corrections which have to be applied for complex formation and hydrolysis, its effect can be disregarded. Thus, the total concentration in solution C_{Zr} will be given by:

$$C_{Zr} = Zr^{4+} + ZrSO_4^{2+} + Zr(SO_4)_2 + Zr(SO_4)_3^{2-} + Zr(OH)^{3+} + Zr(OH)_2^{2+} + Zr(OH)_3^{+}. \quad (13)$$

Substituting in Eq. (13) the value of each component found from Eqs. (7)-(12), we get:

$$C_{Zr} = Zr^{4+} + \frac{K_1[HSO_4^-][Zr^{4+}]}{h} + \frac{K_1K_2[HSO_4^-]^2[Zr^{4+}]}{h^2} + \frac{K_1K_2K_3[HSO_4^-]^3[Zr^{4+}]}{h^3} + \frac{K_4K_5[Zr^{4+}]}{h^2} + \frac{K_4K_5K_6[Zr^{4+}]}{h^3}. \quad (14)$$

After the usual transformations we find the value of Zr^{4+}:

$$Zr^{4+} = \frac{C_{Zr}h^3}{h^3 + K_1[HSO_4^-]h^2 + K_1K_2[HSO_4^-]^2h + K_1K_2K_3[HSO_4^-]^3 + K_4h_2 + K_4K_5h + K_4K_5K_6}. \quad (15)$$

The concentration of hydrogen ions and HSO_4^- ions is calculated in each case on the basis of the formula and Luter's tables [8], in accordance with the accurately measured amounts of sulfuric acid introduced into the solutions (columns 7 and 8, Table 1). On the basis of the total concentration of zirconium found in the filtrate, the ionic concentration $[Zr^{4+}]$ in each of the experiments carried out was calculated by means of formula (15).

Knowing the original amount of zirconium and cupferron, the zirconium content of the filtrate, and the acidity of the original solution, the equilibrium concentrations of nitrosophenylhydroxylamine were calculated, assuming that the latter is found in the form of the undissociated molecule. From the equilibrium concentrations $[H^+]$, $[Zr^{4+}]$, and [HR], the equilibrium constants of the reaction ($K_{eq.}$) were calculated, and, using formula (5), the solubility product (L_s) calculated. The experimental results and the calculated values are given in the table.

Determination of $K_{eq.}$ for Precipitation of Zirconium by Cupferron. Volume of Filtrate 50 ml

Zirconium taken, mg	Cupferron introduced, mg	H_2SO_4 concentration, mole/liter	Zirconium determined in filtrate			Equilibrium concentrations, mole/liter, $K_s = 3.36 \cdot 10^{19}$				$K_s \cdot 10^{19}$
			aliquot, ml	imp/min in the aliquot	total, mg	$[HSO_4^-]$	$[H^+]$	$[Zr^{4+}] \cdot 10^9$	$[HR] \cdot 10^4$	
5	35	0.25	2.5	8024	0.390	0.220	0.280	3.14	4.70	4.01
10	70	0.50	2.0	11456	0.696	0.462	0.538	4.52	8.64	3.33
5	38	0.25	5.0	5062	0.123	0.220	0.280	1.03	7.10	2.35
5	38	0.50	2.0	7835	0.476	0.462	0.538	3.08	9.30	3.64
10	76	0.50	2.0	4940	0.300	0.462	0.538	1.95	12.90	1.55
5	39	0.27	5.0	3457	0.084	0.243	0.297	0.61	7.15	4.88
5	39	0.54	2.0	6419	0.390	0.510	0.570	2.29	9.84	4.92
5	44	0.25	25.0	1220	0.0059	0.220	0.280	0.05	12.80	4.58
5	44	0.50	10.0	7819	0.095	0.462	0.538	0.61	13.7	3.90
5	44	1.00	1.0	9053	1.10	0.945	1.055	14.7	22.5	0.41

In accordance with formula (2), the zirconium concentration should change in proportion to the fourth power of the hydrogen-ion concentration (for a constant concentration of the precipitant) and should be inversely proportional to the fourth power of the precipitant concentration (for a constant hydrogen-ion concentration).

From the results given in the table (taking into account the corrections for hydrolysis and formation of sulfate complexes) it is clear that the values obtained correspond to the given law.

From the results given in the table, it is clear that in most experiments, the values for $K_{eq.}$ differ from the mean value by not more than 1.5-2 times. Taking into account that the value of $K_{eq.}$ is very large ($3.36 \cdot 10^{19}$), such a deviation cannot give an error during the calculation of the solubility product

$$L_s = \frac{K_S^4}{K_{eq}} = \frac{(5{,}3 \cdot 10^{-5})^4}{3{,}36 \cdot 10^{19}} = 2{,}35 \cdot 10^{-37}.$$

A simple comparison of the solubility product of the cupferronates of zirconium ($2.35 \cdot 10^{-37}$) and aluminum ($2.3 \cdot 10^{-19}$) shows that it should be easy to find the optimum conditions for quantitative separation of these two elements.

The solubility of zirconium cupferronate in water can then be calculated from the value found for the solubility product. In view of the very low solubility of zirconium cupferronate, its saturated solutions are extremely dilute, and it is possible to assume that the activity coefficient is equal to one; then, for $L_s = [Zr^{4+}][R^-]^4$ the solubility

$$S_{Zr} = \sqrt[5]{\frac{L_s}{256}} = \sqrt[5]{\frac{2{,}35 \cdot 10^{-37}}{256}} = 1{,}6 \cdot 10^{-8} \text{ mole/liter.}$$

When the work described here was finished, the results of the work carried out by Elving and Olson was published [9]. These authors studied the solubility of the inner-complex compounds of the metals of the fourth group with aromatic nitrosohydroxylamines. Their method consisted in determining the nitrosophenylhydroxylamine concentration of the filtrate polarographically (in a nitrogen stream), after equilibrium has been established between the cupferronate and the solution of the acid. According to their results, the solubility of zirconium cupferronate is $2.3 \cdot 10^{-8}$ mole/liter. The agreement with our result ($1.6 \cdot 10^{-8}$ mole/liter) is quite satisfactory.

Using the equilibrium constants, it should be possible to carry out approximate calculations of the solubility of zirconium cupferronate, under the conditions used for precipitation, as a function of the concentration of acid and excess precipitant in solution.

SUMMARY

The equilibrium constant of the precipitation of zirconium with cupferron has been determined; it was found to be $3.36 \cdot 10^{19}$. The solubility product ($2.35 \cdot 10^{-37}$) and the solubility of zirconium cupferronate were calculated on the basis of the equilibrium constant. The value found for the solubility, $1.6 \cdot 10^{-8}$ mole/liter, agrees satisfactorily with published results.

LITERATURE CITED

[1] K. Schröder, Z. anorg. Chem. 72, 89 (1911).

[2] G. Lundel and H. Knowless, Ind. Eng. Chem., Anal. Ed. 12, 344 (1920).

[3] A. Pinkus and F. Martini, J. de Chem. Phys. 24, 83, 137 (1926).

[4] L.V. Pyatnitskii, Zhur. Anal. Khim. 1, 57 (1946).

[5] R. Connick and W.H. McVey, J. Am. Chem. Soc. 71, 3182 (1949).

[6] A.S. Solovkin, Zhur. Neorg. Khim. 2, 611 (1957).

[7] R. Connick and W. Reas, J. Am. Chem. Soc. 73, 1171 (1951).

[8] R. Luter, Z. Electrochem. 14, 828 (1928).

[9] P. Elving and E. Olson, J. Am. Chem. Soc. 78, 17, 4206 (1956).

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THE EFFECT OF CERTAIN IONS ON THE PRECIPITATION OF URANYL FERROCYANIDE FROM AQUEOUS SOLUTIONS

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In a previous paper [1] results were given of a study by the method of amperometric titration of the conditions for the precipitation of uranyl ions from aqueous solutions by potassium ferrocyanide, while the solubility of the precipitate formed $K_4(UO_2)_4[Fe(CN)_6]_3$ was also determined.

The most favorable medium for the amperometric titration of uranyl by ferrocyanide is a 1 M solution of potassium nitrate at a pH of 3.0-5.0, while the titration temperature should be 40-60°.

In view of the capacity of ferrocyanide to give precipitates with many multivalent cations, the composition of which depends on the anions and univalent cations present in solution, it was of interest to study the effect of a number of salts on the amperometric titration of uranyl by ferrocyanide.

Cations. a) Univalent Me^+. In order to evaluate the effect of ammonium and sodium ions on the results of amperometric titration, titration of uranyl nitrate was carried out in the presence of potassium nitrate on the one hand, and ammonium or sodium nitrate on the other. On replacing from 0 to 100% of the potassium nitrate with ammonium or sodium nitrate, the equivalence point, and, consequently, the molecular ratio $UO_2^{2+}/Fe(CN)_6^{4-}$ remained almost unchanged.

b) Divalent Me^{2+}. Of the divalent metals, zinc, copper, nickel, and lead ions form the least-soluble ferrocyanides. Since the solubility of uranyl ferrocyanide is also very low, it was of interest to establish the sequence in which the precipitates of these ferrocyanides are formed.

Zinc. In a 1 M potassium nitrate solution, zinc ions are clearly titrated by ferrocyanide with formation of a white precipitate of $K_2Zn_3[Fe(CN)_6]_2$. When uranyl ions are present during the titration, initially, a white precipitate of the zinc compound separates out; this subsequently acquires a brown color as a result of the uranyl ferrocyanide that is precipitated.

At the equivalence point, the amount of ferrocyanide used up is equal to the sum of the equivalents of zinc and uranyl, which are calculated from the molar ratios: $Zn^{2+}/Fe(CN)_6^{4-} = 1.5$; $UO_2^{2+}/Fe(CN)_6^{4-} = 1.33$.

The titration curves obtained thereby have the usual shape. All this indicates that when zinc and uranyl ions are present together, the titration proceeds quantitatively, without any change in the composition of these ferrocyanides.

Copper. Titration proceeds differently in the presence of copper ions. Copper ions give precipitates with ferrocyanide which are similar in color to that of the uranyl ferrocyanide precipitate, so that it is not possible to observe visually the sequence in which they are formed.

Both in the pure forms and in mixtures with uranyl ions, copper ions give clearly defined titration curves on titration with ferrocyanide.

As is evident from Table 1, during titration of a solution containing copper alone, ferrocyanides of variable composition are formed when the copper content is low.

For copper contents greater than 0.06 millimole, the precipitate acquires a constant composition, in which the ratio $Cu^{2+}/Fe(CN)_6^{4-} = 1.5$. The double ferrocyanide salt $K_2Cu_3[Fe(CN)_6]_2$ could correspond to this ratio.

The presence of uranyl ions does not affect the molecular ratio

$$\Sigma (Cu^{2+} + UO_2^{2+})/Fe(CN)_6^{4-} = 1{,}5,$$

as long as there is more than 5 millimole Cu^{2+} for one millimole UO_2^{2+}.

At lower copper contents the molar ratio $(UO_2^{2+} + Cu^{2+})/[Fe(CN)_6]^{4-}$ acquires a value approximating to 1.33, which is characteristic of the double salt of uranyl with potassium ferrocyanide:

$$K_4(UO_2)_4[Fe(CN)_6]_3.$$

The constancy of the molar ratios in the precipitates indicates that Cu^{2+} and UO_2^{2+} ions are capable of mutual isomorphous substitution, and consequently the composition of the ternary salt can be expressed in the first case by:

$$K_2(Cu, UO_2)_3[Fe(CN)_6]_2;$$

and in the second case by:

$$K_4(Cu, UO_2)_4[Fe(CN)_6]_3.$$

TABLE 1

Results of the Amperometric Titration of Solutions of Uranyl and Copper by Means of Ferrocyanide

Taken, millimole		Molar ratio	$K_4Fe(CN)_6$ used, mmole	Molar ratio	Composition of salt corresponding to given ratio
Cu^{2+}	UO_2^{2+}	Cu^{2+}/UO_2^{2+}		$\Sigma(Cu^{2+}+UO_2^{2+})$ / $Fe(CN)_6^{4-}$	
0	0,01	0 : 1	0,0078	1,29	$K_4(UO_2)_4 \cdot [Fe(CN)_6]_3$
0,01	0,1	1 : 10	0,0840	1,27	
0,01	0,05	1 : 5	0,0465	1,29	
0,01	0,02	1 : 2	0,0232	1,29	
0,01	0,01	1 : 2	0,0232	1,29	$K_4(Cu, UO_2)_4 \cdot [Fe(CN)_6]_3$
0,01	0,01	1 : 1	0,0145	1,37	
0,01	0,01	1 : 1	0,0145	1,37	
0,01	0,01	2 : 1	0,0224	1,34	
0,03	0,01	3 : 1	0,0290	1,37	
0,05	0,01	5 : 1	0,0370	1,63	
0,10	0,01	10 : 1	0,0750	1,47	$K_2(Cu, UO_2)_3 \cdot [Fe(CN)_6]_2$
0,15	0,01	15 : 1	0,0960	1,55	
0,06	—	6 : 0	0,0415	1,45	
0,10	—	10 : 0	0,0663	1,51	
0,20	—	20 : 0	0,1280	1,56	$K_2Cu[Fe(CN)_6]_2$
0,30	—	30 : 0	0,1940	1,55	

Nickel. Nickel ions are readily titrated with ferrocyanide to form a white precipitate. The molar ratio $Ni^{2+}/Fe(CN)_6^{4-} = 1.29$ at the equivalence point in this case; this corresponds to the double salt $K_4 \cdot Ni_4[Fe(CN)_6]_3$.

When a mixture of Ni^{2+} and UO_2^{2+} ions is titrated, a brown-colored precipitate is formed. The ferrocyanide used up is equal to the sum of the amounts required for the titration of each ion separately. The ratio $\Sigma(Ni^{2+} + UO_2^{2+})/[Fe(CN)_6]^{4+}$ has a mean value of 1.33 ± 0.10, i.e., it has the same value as that obtained during the titration of pure uranyl.

The fact that the composition of the double salts of the ferrocyanides of nickel and uranyl is the same prevents one from solving the question of the sequence in which the double salts are formed, or whether a ternary salt $K_4(Ni, UO_2)_4[Fe(CN)_6]_3$ is formed at the same time.

Lead. The titration curves obtained during the titration of a solution of a pure lead salt are not so clearly defined.

At low concentrations (0.01 millimole in 10 ml) of lead, during titration there is observed the phenomenon of supersaturation, so that the white precipitate of lead ferrocyanide is only formed on addition of a certain excess of $K_4Fe(CN)_6$. The appearance of a precipitate is accompanied by a sharp drop in the diffusion current.

To an accuracy of up to 10%, the molar ratio $Pb^{2+}/[Fe(CN)_6]^{4-} = 2.1 \pm 0.20$, which corresponds to the formula for a simple salt $Pb_2 \cdot Fe(CN)_6$. During titration of a mixture of Pb^{2+} and UO_2^{2+} ions there is formed a brownish precipitate, in which the mean molar ratio $\Sigma(Pb^{2+} + UO_2^{2+})/[Fe(CN)_6]^{4-} = 2.0 \pm 0.10$. The apparently incomprehensible effect shown by lead can be clarified if one assumes that the lead ions replace the potassium ions in the double salt, with formation of the compound: $Pb_2(UO_2)_4[Fe(CN)_6]_3$, while the excess lead ions form a simple ferrocyanide.

Such an assumption would appear to be possible if one bears in mind the similarity of the ionic radii of lead and potassium.

Attempts to eliminate interference on the part of the divalent metals listed, by masking them with sodium ethylenediaminetetracetate (EDTA-Na), did not give positive results.

Addition of EDTA-Na in amounts which were twice and three times that necessary with respect to the equivalent amount of these metals, led to their complete masking as a result of the formation of compounds which are more stable than ferrocyanides.

However, EDTA-Na when present in excess amounts completely complexes UO_2^{2+} so that amperometric titration of the latter becomes impossible.

TABLE 2

Amperometric Titration of Uranium in the Presence of Aluminum, Chromium, and Cerium

Taken, mmole				Molar ratio M^{n+}/UO_2^{2+}	$K_4Fe(CN)_6$ used, ml	Note
Al^{3+}	Cr^{+}	Ce^{3+}	UO_2^{2+}			
—	—	—	0,01	0 : 1	0,80	
0,10				1 : 0	Not titrated	
0,50				5 : 0	"	
0,01			0,01	1 : 1	0,90	Titration curves clearly defined
0,05	—	—	0,01	5 : 1	0,90	
0,10	—	—	0,01	10 : 1	0,88	
0,30	—	—	0,01	30 : 1	0,90	
0,50	—	—	0,01	50 : 1	0,90	
0,80			0,01	80 : 1	1,00	Titration curves not clearly defined
1,00	—	—	0,01	100 : 1	1,00	
—	0,01	—	—	1 : 1	Not titrated	
—	0,05			5 : 1	"	
—	0,01	—	0,01	1 : 1	0,85	Titration curve not completely clearly defined
—	0,02	—	0,01	2 : 1	0,80	
—	0,03		0,01	3 : 1	0,80	
—	0,05		0,01	5 : 1	0,80	
—	—	0,005	—	0 : 0,5	Not titrated	
—	—	0,010	—	0 : 1	"	
—	—	0,0025	0,01	0,25 : 1	0,85	Titration curves clearly defined
—	—	0,0050	0,01	0,5 : 1	0,85	
—	—	0,010	0,01	1 : 1	0,85	
—	—	0,025	0,01	2,5 : 1	0,90	
—	—	0,050	0,01	5,0 : 1	0,95	

c) Trivalent Me^{3+}. Aluminum, chromium (III), cerium (III). Aluminum (III), chromium (III), and cerium (III) ions are not titrated in 1 M KNO_3 solution at a pH of 4.0-5.0 by ferrocyanide. Solutions containing the ions listed in amounts up to 0.1 millimole in 10 ml and a small excess of ferrocyanide do not give precipitates. When these ions are present together with uranyl ions in solution, precipitates of uranyl ferrocyanide of the normal type are formed.

The composition of the ferrocyanide precipitate does not change. This follows, as is evident from Table 2, from the fact that the amount of ferrocyanide used up at the equivalence point remains almost the same whether uranium alone is titrated or whether it is titrated together with the elements listed. The influence of these ions is only manifested in the rate at which the precipitate of uranyl ferrocyanide is formed; this leads to distortion of the lower part of the titration curves and renders establishment of the equivalence point difficult.

As indicated in Table 2, the titration curves still have a normal shape as long as the content of the elements listed does not exceed the uranium content by more than 50 times in the case of aluminum, 3-4 times in the case of chromium, and by more than 5 times in the case of cerium.

Iron. Iron (III) ions form a precipitate of Prussian blue with ferrocyanide in a potassium nitrate solution. The solubility of this compound is less than that of uranyl ferrocyanide. This follows from the fact that during titration of a mixture of these ions, initially, a blue precipitate of iron is formed; subsequently, as the brown precipitate of uranyl ferrocyanide is formed, the iron ferrocyanide acquires a greenish shade.

Iron (III) present in any amounts increases the results of the amperometric titration of uranyl.

It might be expected that iron (II) ions will not interfere with the titration of uranium in view of the comparatively high solubility of iron (II) ferrocyanide.

However, in a pure solution of 1 M potassium nitrate at a pH of 3.5-5.0, it is difficult to establish conditions under which iron (II) ions are not oxidized to the trivalent state.

Iron can only be kept in the divalent state in the presence of a reducing agent or complexing agents.

Ascorbic acid and hydroxylamine hydrochloride were tested as reducing agents. We were unable to use them, since ascorbic acid complexes uranyl fairly strongly and depresses the titration results, while hydroxylamine hydrochloride did not reduce the ferric ions completely.

Negative results were also obtained when EDTA-Na and potassium fluoride were tried.

d) Quadrivalent Me^{4+}. Thorium (IV). In a supporting electrolyte of potassium nitrate, thorium is clearly titrated with ferrocyanide to form a white precipitate which does not separate out readily.

TABLE 3

Amperometric Titration of Thorium with Potassium Ferrocyanide

Taken, mmole		$K_4Fe(CN)_6$ used, mmole	$Th^{4+}/Fe(CN)_6^{4-}$	$\Sigma(Th+UO_2^{2+})/Fe(CN)_6^{4-}$
Th^{4+}	UO_2^{2+}			
0,00395	—	0,00436	0,905	—
0,00395	—	0,00340	1,165	—
0,00395	—	0,00436	0,900	—
0,00790	—	0,00680	1,160	—
0,00790	—	0,00680	1,160	—
0,00790	—	0,00680	1,160	—
0,00790	—	0,00820	0,960	—
0,0158	—	0,0145	1,090	—
0,0158	—	0,0145	1,090	—
0,0236	—	0,0208	1,170	—
0,0236	—	0,0232	1,010	—
		Mean	1,060	
—	0,010	0,0068		1,33
0,00395	0,010	0,0097		1,45
0,00790	0,005	0,0097		1,32

It follows from Table 3 that the ferrocyanide has the composition $ThFe(CN)_6$.

During titration of a mixture of uranyl and thorium ions, the first and subsequent drops of ferrocyanide lead to the appearance of a brown precipitate.

The volume of ferrocyanide solution is equal to the sum of the volumes of ferrocyanide required for the titration of each element taken separately.

No additional breaks are observed on the titration curves.

These observations indicate that the ferrocyanides of uranyl and thorium have roughly the same solubility, and that they are precipitated simultaneously during titration.

Anions. The effect of the following anions was studied: chloride, sulfate, phosphate, vanadate, molybdate, and chromate.

Chlorides. On replacing from 0 to 50% of the NO_3^- ions in a 1 M solution of potassium nitrate by an equivalent amount of chloride ions, it was established that the presence of chloride ions does not affect amperometric titration of uranium with ferrocyanide.

Sulfates. Satisfactory results are obtained on carrying out amperometric titration at room temperature, even when the potassium nitrate is completely replaced by potassium sulfate. Compared with a pure solution of potassium nitrate, titration proceeds considerably more slowly. Sulfate ions show a marked effect on increasing the temperature. It has been established previously [1] that, in the presence of sulfates, the solubility of the uranyl ferrocyanide precipitate increases sharply with increasing temperature. Thus, ferrocyanide which has been precipitated in the cold will dissolve completely on increasing the temperature to 80-90°, and will settle out again on cooling. This is of decisive importance for the amperometric titration of uranium carried out at 40-60°, even in those cases where the sulfate-ion content does not exceed 10% of the amount of potassium nitrate in solution.

It was noticed that at elevated temperatures, when sulfate ions are present in solution, the platinum electrode is readily passivized and loses its sensitivity. Under such conditions the platinum surface becomes covered with a blue film. The sensitivity of the electrode can be restored by treating the surface with alkali and nitric acid.

Phosphates. Uranyl ions are quantitatively precipitated by phosphate ions from a 1 M potassium nitrate solution at pH 3.0-5.0. Under the conditions used for amperometric titration, the solubility of the phosphate is less than the solubility of the uranyl ferrocyanide, as a consequence of which, the experimental results obtained for uranium are strongly depressed. Attempts to mask phosphate ions by means of magnesium ions, which themselves do not interfere with the titration, did not give positive results.

TABLE 4. Amperometric Determination of Uranium in the Presence of Vanadate

VO_3 taken, mmole	UO_2^{2+} taken, mmole	Ratio VO_2^-/UO_2^{2+}, mmole	$K_4Fe(CN)_6$ used, ml	VO_3 taken, mmole	UO_2^{2+} taken, mmole	Ratio VO_2^-/UO_2^{2+}, mmole	$K_4Fe(CN)_6$ used, ml
–	0.010	0:1	0.80	0.03	0.010	8:1	0.75
0.02	–	2:0	Not titrated	0.08	0.010	8:1	0.80
0.08	–	8:0	" "	0.16	0.010	16:1	0.85
0.20	–	20:0	" "	0.40	0.015	27:1	1.27
0.80	–	80:0	" "	0.40	0.15	27:1	1.25
0.04	0.010	4:1	0.80	0.40	0.010	40:1	0.85
0.04	0.010	4:1	0.80	0.40	0.010	40:1	0.90

Vanadates. Vanadate ions present in a 1 M potassium nitrate solution at pH 4.0-5.0 do not interfere with amperometric determination.

As is evident from Table 4, satisfactory titration results can be obtained even when the amount of vanadate present is 30-40 times that of the uranium present.

Tests showed that it is necessary to control the acidity of the medium rigidly (pH 4.0-5.0) in order to obtain reliable results. At higher pH, precipitation of uranyl is delayed, while at lower pH, the results obtained are high because of the interaction of ferrocyanide and vanadate.

When the pH is sufficiently low, oxidation of ferrocyanide by the vanadate can occur.

The quadrivalent vanadium ions which are formed as a result of this reaction are precipitated by excess ferrocyanide in the form of a yellow precipitate which changes (on standing) subsequently to green.

When the interaction between ferrocyanide and vanadate is carried out in the presence of any reducing agent, e.g., ascorbic acid, formation of the yellow precipitate starts at pH higher than 5.

Thus, if uranium is to be titrated amperometrically in the presence of vanadium, reducing agents must be absent.

The requisite pH can be established by using a mixed indicator, for this purpose an equal number of drops of 0.1% solutions of methyl orange (aqueous solution) and bromophenol blue (alcoholic solution) are added to the test solution.

The final color of the test solution is compared with the color of a buffer solution with a pH of 4.5.

Molybdate. In the pH range 3.0 to 5.0, molybdate does not react with ferrocyanide, but reacts with uranyl ions, precipitating them in the form of uranyl molybdate. Low results are obtained during amperometric titration of uranium in the presence of molybdate ions.

Chromate. At pH 3-5, chromate ions do not oxidize ferrocyanide and do not interfere with amperometric titration.

At lower pH values, oxidation of ferrocyanide occurs. At pH about 1.0, chromate can be quantitatively titrated with ferrocyanide.

This study of the effect of certain ions on the amperometric titration of uranium with ferrocyanide allows one to divide all the elements tested into the two following groups:

Ions which interfere with uranium determination	Ions which do not interfere with uranium determination
Zinc	Ammonium
Copper	Sodium
Nickel	Magnesium
Lead	Aluminum
Iron (III)	Chromium (III)
Thorium	Cerium (III)
Phosphates	Chlorides
Molybdates	Vanadates
Sulfates (partially)	Chromates

The experiments which we have carried out confirm once again the general opinion regarding the complexity of the chemistry of the ferrocyanides.

The amperometric-titration method has shown itself to be a convenient means for studying the reaction products obtained during the interaction of ferrocyanide with various ions.

A study of the interaction of ferrocyanides with the oxy ions of vanadium, molybdenum, chromium, etc., should obviously be of special interest. Thanks to the work, mainly of L.V. Tananaev et al. and O.A. Songina, the question of the interaction of ferrocyanide with divalent metal ions has been dealt with in the literature. On the other hand, the interactions of ferrocyanide with the oxy ions has hardly been touched upon in the literature, although the study of such interactions could lead to the development of new methods for determining them.

The results which we have obtained by means of amperometric titration on the composition of the precipitates of the binary salts of potassium ferrocyanide with divalent metal ions agree with the results obtained by other methods.

Thus, the precipitate of zinc ferrocyanide corresponds in its composition to the generally accepted formula: $K_2Zn_3[Fe(CN)_6]_2$.

The composition of the precipitate of lead ferrocyanide $Pb_2[Fe(CN)_6]$ agrees with the results of Treadwell [2] and Songina [3].

The composition of the nickel salt $K_4Ni_4[Fe(CN)_6]$ agrees with the results of Tananaev and Levina [4].

The composition of the double copper salt $K_2Cu_3[Fe(CN)_6]_2$ does not confirm the results of Chovnyk and Kleibs [5] and Chovnyk and Kuz'mina [6], but agrees with the results of Tananaev and Glushkova [7], who found a similar compound for the double salt of copper and thallium.

Our results on the composition of thorium ferrocyanide $ThFe(CN)_6$ agree with those of Glushkova [8], while our results on the mixed ferrocyanide of uranyl and potassium $K_4(UO_2)_4[Fe(CN)_6]_3$ agree with those of Tananaev and Levina [9].

Of special importance is the participation of uranyl ferrocyanide in the formation of ternary salts with copper, nickel, and lead. Copper ferrocyanide belongs to the class of very sparingly soluble compounds. Accordingly, isomorphous substitution of part of the copper by uranyl may prove to be a means for the quantitative separation of uranium. This could be all the more useful since uranium can be readily separated from copper and ferrocyanide by treating the precipitate obtained with ammonia.

The very clearly defined curves obtained during the amperometric titration of thorium with ferrocyanide could be used as a basis for the quantitative determination of thorium, especially, as we have shown, since cerium (III) salts are not titrated under these conditions.

SUMMARY

The effect of certain cations and anions on the composition of the precipitate formed by the interaction of uranyl and ferrocyanide ions has been studied by amperometric titration.

It has been shown that NH_4^+, Na^+, Mg^{2+}, Al^{3+}, Cr^{3+}, Ce^{3+}, VO_3^-, CrO_4^-, and Cl^- do not alter the composition of uranyl ferrocyanide $K_4(UO_2)_4[Fe(CN)_6]_3$ and do not interfere with the titration, while Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Fe^{3+}, Th^{4+}, MoO_4^{2-}, PO_4^{3-}, SO_4^{2-} interfere with the titration, forming, in some cases, more complicated compounds.

LITERATURE CITED

[1] V.G. Sochevanov, N.V. Shmakova, and G.A. Volkova, Zhur. Neorg. Khim. 2, 2049 (1957).

[2] V. Treadwell and E. Shervet, Helv. Chim. Acta 5, 633 (1922); 6, 550 (1928).

[3] O.A. Songina, Zavodskaya Lab. 11, 1237 (1952).

[4] I.V. Tananaev and M.P. Levina, Zhur. Anal. Khim. 1, 224 (1946).

[5] N.T. Chovnyk and G.A. Kleibs, Zhur. Anal. Khim. 3, 303 (1948).

[6] N.T. Chovnyk and N.N. Kuz'mina, Zhur. Anal. Khim. 4, 97 (1949).

[7] I.V. Tananaev and M.A. Glushkova, Zhur. Neorg. Khim. 2, 586 (1957).

[8] M.A. Glushkova, "Mixed ferrocyanides of thallium," Thesis, (Moscow IONKh AN SSSR), 1955.

[9] I.V. Tananaev and M.I. Levina, Zhur. Neorg. Khim. 3, 2045 (1958).

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DETERMINATION OF URANIUM BY AMPEROMETRIC TITRATION

V.F. Eskevich and L.A. Komarova

Uranium has been titrated amperometrically by a number of authors [1-5]. Kolthoff and Johnson [1] titrated uranium with nitrophenylarsonic acid using the diffusion current of uranium and nitrophenylarsonic acid (the wave obtained by the reduction of the nitro group to the amino group). Kolthoff and Kohn [2] have developed a technique for titrating phosphates with a uranium solution using the diffusion current of uranium. Uranium is reduced on a dropping mercury electrode; accordingly, uranium can be titrated amperometrically on a dropping-mercury electrode by many precipitants. Such a method, however, is not sensitive enough.

Amperometric methods which are based on oxidation-reduction reactions are more sensitive. In these cases, titration is usually carried out on a platinum indicator electrode, which permits one to work with such strong oxidizing agents as ammonium vanadate, potassium dichromate, etc.

Amperometric titration of uranium using a platinum electrode is carried out on the basis of the diffusion current of the titrant.

In the work described here, a study was made of the conditions required for the direct amperometric titration of uranium by means of ammonium vanadate using a platinum microelectrode.

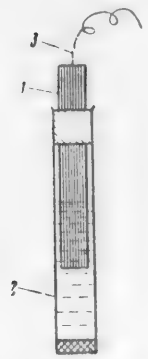

Fig. 1. Bismuth reference electrode: 1) rod of bismuth metal; 2) test tube with porous bottom filled with 12 N H_2SO_4; 3) contact for connecting the electrode to the external circuit.

EXPERIMENTAL

Titration was carried out on a "Gintsvetmet" polarograph with a mirror galvanometer having a sensitivity of $2.4 \cdot 10^9$ amp/mm/m. The indicator electrode was a platinum wire 15 mm long and 0.5 mm in diameter fused into the end of a glass tube. The electrode was rotated at the rate of 750 rpm by means of a synchronous motor. The platinum wire was dipped now and again in a chromic mixture and washed with distilled water.

A bismuth electrode (Fig. 1) was used as the reference electrode.

According to Syrokomskii's results [6], the oxidation-reduction potential of the system V^V/V^{IV} increases with increasing acidity. In 12 N H_2SO_4, it is equal to +1.22 volts. Under these conditions, the reaction between quadrivalent uranium and ammonium vanadate proceeds rapidly.

The anode-cathode curves obtained (Fig. 2) on the platinum electrode indicate that ammonium vanadate in 12 N sulfuric acid gives a clearly defined diffusion current in the range +0.2 to −0.2 volts with respect to the saturated calomel electrode (or from +0.18 to −0.22 volts with respect to the bismuth electrode).

The maximum diffusion current occurs at 0-0.2 volts as is evident from Fig. 2; accordingly, titration can be carried out without applying an external potential, and this appreciably simplifies the apparatus.

A study of the effect of the acidity of the medium on the nature of the anode-cathode curves for ammonium vanadate showed that, within the limits 8 to 16 N, there is no change in the nature of the curves.

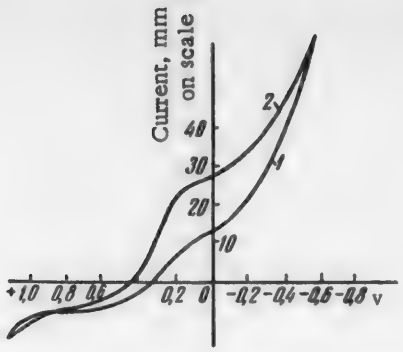

Fig. 2. Anode-cathode curves for ammonium vanadate in 12 N H_2SO_4: 1) 0.001 N NH_4VO_3; 2) 0.01 N NH_4VO_3.

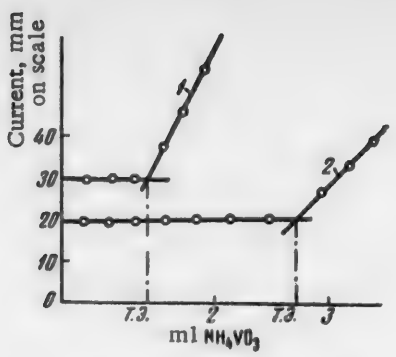

Fig. 3. Curves obtained during titration of 0.200 mg uranium with ammonium vanadate: 1) 0.001 N NH_4VO_3; 2) 0.000* N NH_4VO_3; galvanometer sensitivity 1/10.

TABLE 1

Comparative Titration of Quadrivalent Uranium After Phosphate Precipitation

Vanadate concentration	Uranium introduced, mg	NH_4VO_3 used, ml		Uranium found, mg		Absolute error, mg		Relative error, %	
		Amperometrically	Using indicator	Amperometrically	Using indicator	Amperometrically	Using indicator	Amperometrically	Using indicator
0,001	0,2	1,50	2,00	0,179	0,238	−0,021	+0,038	−10,5	+19
		1,50	2,10	0,179	0,250	−0,021	+0,050	−10,5	+25
		1,50	2,05	0,179	0,244	−0,021	+0,044	−10,5	+22
		1,50	2,10	0,179	0,250	−0,021	+0,050	−10,5	+25
		1,50	2,00	0,179	0,238	−0,021	+0,038	−10,5	+15
				Mean		−0,021	+0,044	−10,5	+22
0,001	0,1	0,78	1,05	0,093	0,125	−0,007	+0,025	−7	+25
		0,76	1,05	0,091	0,125	−0,009	+0,025	−9	+25
		0,76	1,05	0,091	0,125	−0,009	+0,025	−9	+25
		0,77	1,05	0,092	0,125	−0,008	+0,025	−8	+25
		0,78	—	0,093	0,125	−0,007	—	−7	+25
				Mean		−0,008	+0,025	−8	+25
0,0002	0,025	1,00	—	0,0239	—	−0,0011	—	− 4,4	—
		1,10	—	0,0262	—	+0,0037	—	+14,8	—
		1,15	—	0,0273	—	+0,0048	—	+19,2	—
				0,0239	—	−0,0011	—	− 4,4	—
				Mean		+0,0005	—	+ 4,0	—
0,0002	0,0125	0,54	—	0,0128	—	+0,0003	—	0,0	—
		0,53	—	0,0126	—	+0,0001	—	+0,8	—
		0,56	—	0,0133	—	+0,0008	—	+6,4	—
				0,0133	—	+0,008	—	+6,4	—
				Mean		+0,0005	—	+4,0	—
0,0002	0,0062	0,26	—	0,0062	—	0,0000	—	+0,0	—
		0,28	—	0,0067	—	+0,0005	—	+8,0	—
		0,27	—	0,0065	—	+0,0003	—	+4,8	—
		0,27	—	0,0065	—	+0,0003	—	+4,8	—
		0,26	—	0,0062	—	+0,0000	—	+0,0	—
				Mean		+0,0002	—	+3,5	—

*As in the original — Publisher's note.

The largest potential jump during the potentiometric titration of uranium with ammonium vanadate, and the sharpest break on the amperometric curve are obtained in 8-16 N sulfuric acid.

In Fig. 3 are shown the curves obtained during titration of 0.200 mg of uranium with ammonium vanadate solution in 12 N sulfuric acid.

In order to evaluate the sensitivity of the method, uranium was reduced in a bismuth reducer or by means of electrolysis on a mercury cathode, and then titrated with ammonium vanadate in 12 N sulfuric acid. The total volume of solution was 25 ml. As a result of these experiments, it was established that even on titrating such small amounts as 25 γ – 1 mg of uranium the relative error was only 2-3%.

The method was checked on production samples. The samples were prepared by the hydrosulfite-phosphate or by the chromo-phosphate methods [7].

Table 1 contains the results obtained on titrating pure solutions of uranium with ammonium vanadate after preparing the samples by the hydrosulfite-phosphate method. They show that amperometric titration is definitely superior to an indicator method; when an indicator is used, the results are much too high, the results being higher the less the amount of uranium being titrated.

TABLE 2

Determination of the Uranium Content of Coal Cakes by Amperometric Titration

Uranium cont. of aliquot of sample,* mg	Uranium introduced, mg	Tot. uranium cont., mg	Uranium found, mg	Error	
				Abs., mg	Rel., %
0,118	0,05	0,168	0,169	+0,001	+0,6
0,042	0,05	0,092	0,095	—0,003	+3,26
0,495	0,05	0,545	0,535	—0,010	—1,84
0,034	0,05	0,084	0,082	—0,002	—2,38
0,035	0,05	0,085	0,082	—0,003	—3,52
0,057	0,05	0,107	0,111	+0,004	+3,61
0,033	0,05	0,083	0,085	+0,002	+2,35
0,045	0,05	0,095	0,095	—0,000	0,00
0,043	0,05	0,093	0,093	0,000	0,00
5,80	0,05	5,85	6,25	+0,400	+6,83

*Determined amperometrically.

Table 2 contains results obtained by amperometric determination of uranium in coal cakes, with and without addition of uranium prior to decomposition of the samples: to an aliquot of cake (0.5 g) was added 0.5 mg uranium (1 ml of a solution containing 0.5 mg uranium/ml); the sample was then processed further by the hydrosulfite-phosphate or the chromo-phosphate methods.

Amperometric titration was applied to the determination of uranium in wastes from technological processing and in production solutions. The results were compared with those obtained on titrating with an indicator (phenylanthranilic acid and barium diphenylaminosulfonate).

TABLE 3

Amperometric Determination of Uranium in Standard Ores

Specified uranium content, %*	Uranium found, %*
0,072±0,003	0,070±0,0003
0,237±0,003	0,236±0,002
0,103±0,002	0,098±0,001
0,059±0,004	0,059±0,001
0,081±0,004	0,084±0,003

*All the samples were air dry.

Application of amperometric titration to the analysis of production samples showed that the use of amperometric titration instead of titration by means of an indicator in the hydrosulfite-phosphate and chromo-phosphate methods leads to a considerable increase in both the sensitivity and accuracy of the method.

The method was checked on standard samples of uranium ores (Table 3).

Analytical procedure. The amount of sample taken depends on the uranium content: for 1-0.01% U the sample taken should be 0.2-0.5 g, and the strength of the ammonium vanadate solution 0.01 N; for 0.1-0.01% U, the sample should be 0.5-1 g and the strength of the ammonium vana-

date 0.01 N; for 0.01-0.0005% U, the sample should be 1 g and the strength of the ammonium vanadate 0.0002 N. The sample is given a preliminary chemical treatment by the hydrosulfite-phosphate or the chromo-phosphate methods [7]. After decomposition of the ores and removal of the insoluble part, the acid solution is neutralized with ammonia using methyl yellow (pH 2.3) as indicator, 3 ml of concentrated hydrochloric acid is then added and the solution diluted to 200 ml. To this solution is added 10 ml of a 10% solution of disodium hydrogen phosphate, sodium hydrosulfite (1 g per g of sample), 3-4 ml of thorium chloride (5 mg of thorium per ml),and a small amount of paper pulp. After coagulation, the precipitated phosphates of uranium and coprecipitant are filtered under vacuum through a No. 3 filter funnel with porous glass or through a Buchner funnel ("blue or white band"). The uranium phosphate is dissolved on the filter in 8-16 N sulfuric acid; three to four lots of 10-15 ml of the latter are used, each aliquot being sucked through into a clean flask after 5-10 minutes. The total volume of solution should not exceed 100 ml.

The solution is quantitatively transferred into a 150-200-ml beaker. In the chromo-phosphate variant of the method, after addition of phosphate, 0.5-15 g of solid ammonium thiocyanate is added (on the basis of 2.5 g of ammonium thiocyanate to 0.1 g of iron); this is followed by 0.5 N $CrCl_3$ solution until the red color of ferric thiocyanate disappears; 3 ml of the $CrCl_3$ solution is added in excess. The procedure subsequently followed is the same as that in the hydrosulfite-phosphate method.

Before titrating the test solution the requisite sensitivity of the galvanometer is chosen. This is established by lowering the electrodes into a solution of 12 N sulfuric acid, switching on the motor and galvanometer, and regulating, by means of a corrector, the position of the light spot of the galvanometer so that is is near to the zero of the scale. Then, while adding ammonium vanadate, the requisite sensitivity of the galvanometer is selected by means of a shunt (on adding 0.2 ml of ammonium vanadate the light spot should be displaced 2-4 cm along the scale). Having washed the electrodes with distilled water, they are lowered into the beaker containing the test solution. Ammonium vanadate solution is added to the solution in lots of 0.1-0.2 ml from a microburet, and the position of the light spot on the scale recorded each time. The equivalence point is established graphically.

SUMMARY

It has been shown that uranium (down to 1 γ/ml) can be titrated amperometrically with ammonium vanadate solution with an accuracy of 2-3%. A bismuth electrode is used as a reference electrode. No external potential is applied during titration.

The samples are prepared for titration by the hydrosulfite-phosphate or the chromo-phosphate methods.

LITERATURE CITED

[1] I. Kolthoff and H. Jonson, J. Electrochem. Soc. 55, 138 (1951).

[2] I. Kolthoff and J. Kohn, Ind. Eng. Chem. Anal. Ed. 14, 412 (1942).

[3] K. Rodden, Analytical Chemistry of Uranium and Thorium [Russian translation] (IL, Moscow, 1956).

[4] O.A. Songina, Amperometric Titration in the Analysis of Mineral Raw Materials [in Russian] (Gosgeoltekhizdat, Moscow, 1957).

[5] I. Kolthoff and J. Lingane, Polarography (London, 1952).

[6] V.S. Syrokomskii and Yu.V. Klimenko, Vanadatometry [in Russian] (Metallurgizdat, Sverdlovsk, 1950).

[7] P.N. Palei, Research in Geology, Chemistry, and Metallurgy [in Russian] (Izd. AN SSSR, 1955) p. 21.

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SEPARATION OF URANIUM FROM ACCOMPANYING METALS BY MEANS OF ION-EXCHANGE CHROMATOGRAPHY

D.I. Ryabchikov, P.N. Palei, and Z.K. Mikhailova

Separation of uranium from the elements accompanying it by means of ion-exchange chromatography is based on the relationship between the sorbability of the ions and the sign and value of the charge [1]. The use of the difference in the value of the charge is less effective from a practical point of view: in this way, uranium is separated in the main from some elements U^{VI}–Th; U^{VI}–Fe^{III} [1-3].

In order to separate uranium, use is made of strongly basic anion exchange resins containing quaternary ammonium groups which selectively absorb the chloride [4-6], sulfate [7-8], carbonate [9], and acetate [10] complexes of uranium.

In order to separate uranium from the accompanying elements which are most difficult to separate (V, Mo, Fe^{III}, Cu, and Pb), we thought it would be best to use the difference in the capacity of the elements to form complexes with sodium ethylenediaminetetraacetate (EDTA-Na) [11].

Separation of Uranium from Accompanying Metals in the Presence of EDTA-Na on a Sulfonate Cation Exchange Resin

The ion-exchange resin used was the cation exchange resin KU-2 with a particle size of 0.25 mm; it was prepared according to GOST 5629-52. For each test, 10 ml of the cation exchange resin in the swollen state was used. The column, which was 25 cm long, had a diameter of 1 cm.

In order to establish the conditions necessary for separating the elements, a study was made of their behavior on the KU-2 cation exchange resin in the hydrogen and sodium forms, in the presence of EDTA-Na* at various pH values. EDTA-Na was added to the test solution in equimolar amounts** with respect to the components present; the pH was adjusted by means of ammonia (free from carbonate) using a glass electrode. The solution was passed through the column at the rate of 0.8 cm/minute. The contents of the various elements in the filtrates were determined photocolorimetrically (uranium by the peroxide method, molybdenum by the thiocyanate method; vanadium by the peroxide method, copper by the diethyldithiocarbamate method [13]). Tungsten was determined radiometrically on the basis of a β-count (when the test solution was prepared the W^{185} isotope was introduced); lead was determined polarographically [14]. In those cases where EDTA-Na interfered with determination of the element, it was removed by oxidizing the mixture with concentrated sulfuric and nitric acids.

For comparison, experiments were also carried out on the sorption of vanadium, molybdenum, and tungsten, obtained under similar conditions, but in the absence of EDTA-Na.

The curves in Figs. 1, 2, 3, and 4 illustrate the relation between completeness of sorption of the elements and the acidity of the medium.

Uranyl ions only exist in acid solutions, since at pH > 4.2 diuranates separate out. In the presence of EDTA-Na, this phenomenon is observed at pH > 9.2. With increasing pH of the original solution, sorption of uranium on

*The commercial product was purified by a technique described in [12].

**This procedure was adopted throughout the subsequent experiments.

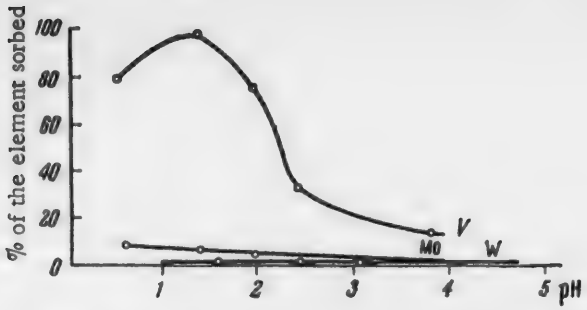

Fig. 1. Relation between the sorption of molybdenum, vanadium, and tungsten and the pH of the medium (cation exchange resin KU-2 in the hydrogen form).

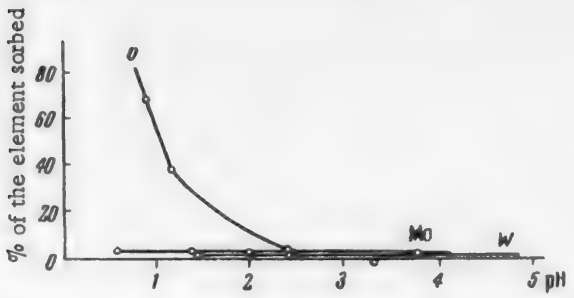

Fig. 2. Relation between the sorption of molybdenum, vanadium, and tungsten and the pH of the medium (cation exchange resin KU-2 in the sodium form).

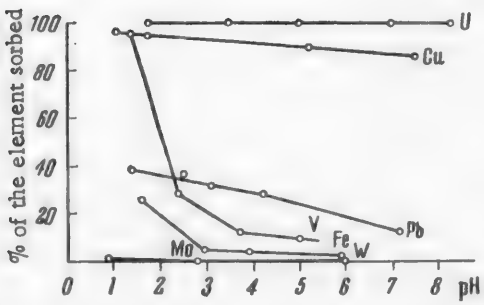

Fig. 3. Relation between pH of the medium and the sorption of uranium, molybdenum, vanadium, tungsten, iron (III), copper, and lead, in the presence of EDTA-Na (cation exchange resin KU-2 in the hydrogen form).

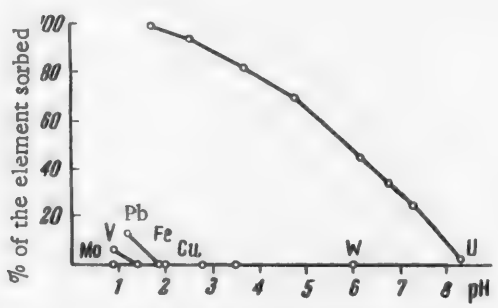

Fig. 4. Relation between the sorption of uranium, molybdenum, vanadium, tungsten, iron (III), copper, and lead, and the pH of the medium, in the presence of EDTA-Na (cation exchange resin KU-2 in the sodium form).

the cation exchange resin in the sodium form decreases, and in media approximating to neutral there is observed considerable (65-90%) breakthrough of the uranium through the column of cation exchange resin into the filtrate (Fig. 4). The latter can be explained by the formation of an anionic complex of uranium in solution.

We have shown earlier [15] that formation of a compound of uranium with EDTA-Na occurs at pH > 3; this does not contradict the results of other authors [16].

In the presence of EDTA-Na, quantitative sorption of uranium on the cation exchange resin in the hydrogen

form, even from neutral solutions (Fig. 3), can only be explained by the breakdown of the complex compound of the acid which is formed as a result of the ion-exchange process. A comparison of the sorbability of Mo, W, and V in the absence (Figs. 1 and 2), and in the presence of EDTA-Na (Figs. 3 and 4), in acid media, showed that in the latter instance sorption is considerably lowered. For example, at pH 0.9 in the absence of EDTA-Na, 27.9% of the vanadium passes into the filtrate (Fig. 2), while in the presence of EDTA-Na, 94.4% passes into the filtrate (Fig. 4). The same phenomenon is observed in the case of molybdenum. Consequently, it can be assumed that, under the conditions indicated, compounds of these elements with EDTA-Na are formed.

Iron, copper, and lead form stable complex compounds of the anionic type with EDTA-Na; naturally, they are not sorbed on the cation exchange resin in the sodium form (Fig. 4).

Comparison of the curves obtained (Figs. 1-4) leads one to assume that, by using the cation exchange resin KU-2 in the sodium form, while the pH of the original solution is 1.7-1.9 and EDTA-Na is present, it should be possible to separate uranium from a large number of accompanying elements.* This assumption was checked on synthetic mixtures, in whose making up we were guided by the typical proportions of the elements in industrial samples.

EDTA-Na was added to synthetic mixtures containing various ratios of the components, and the procedure outlined above then followed. In preparing solutions containing uranium and tungsten, however, after addition of the EDTA-Na and neutralization, the mixture was heated** on a water bath for ten minutes, and after cooling was passed through the cation exchange resin. Molybdenum, vanadium, tungsten, and iron were determined in all the experiments in the combined filtrate and wash liquors.

Uranium was desorbed by means of a 10% solution of HNO_3 (passed through at the rate of 1.6 ml/minute), while the amount of it was determined by the peroxide method; alternatively, it was desorbed with 10% H_2SO_4 and determined vanadometrically [17].

The separation is completely satisfactory (Tables 1 and 2).

TABLE 1

U, mg		Error, %	Mo, mg		Error, %	V, mg		Error, %	W, mg		Error, %
taken	found		taken	found		taken	found		taken	found	
10,0	9,95	—0,5	10,0	10,0	0,0	—	—	—	—	—	—
12,40	12,43	+0,2	1,18	1,16	—1,6	—	—	—	—	—	—
12,40	12,45	+0,4	0,0987	0,099	+0,3	—	—	—	—	—	—
13,4	13,4	0,0	—	—	—	12,5	12,6	+0,8	—	—	—
13,4	13,5	+0,74	—	—	—	1,25	1,24	+0,8	—	—	—
13,4	13,5	+0,74	—	—	—	0,125	0,122	—2,4	—	—	—
15,4	15,25	—0,9	—	—	—	—	—	—	4,0	3,86	—3,5
12,56	12,56	+0	—	—	—	—	—	—	12,0	12,6	+5,0
40,0	39,8	—0,5	—	—	—	—	—	—	2,0	1,98	—1,0

Traces of copper, which were detected in the desorbed uranium solution for an original ratio of $C_U/C_{Cu} = 1$, were found to be very small, and do not essentially affect the results for uranium. Some complications develop only for $C_U/C_{Pb} = 1$; however, we did not come across such ratios in the samples that were analyzed.

The method was tested, first of all, on uranium-rich materials in which the elements accompanying uranium were present in small amounts, namely, in uranium-molybdenum, uranium-tungsten alloys, and in certain concentrates.

An aliquot of test material (0.5 g) was broken down with aqua regia (alloys) or with perchloric acid (concentrates). The solution obtained was transferred into a standard flask (250 ml), and an aliquot of this solution

*The results of the separation of uranium from vanadium and molybdenum on the sulfonate cation exchange resin, as well as individual results given in Tables 1 and 4, were obtained by A.V. Yamshchikov.

**Heating accelerates dissolution of the uranyl tungstate, which is formed initially on pouring the original solutions of the components together, in the absence of EDTA-Na.

TABLE 2

U, mg		Error, %	Fe, mg		Error, %	Cu, mg		Pb, mg	
taken	found		taken	found		taken	found in desorbed uranium solution	taken	found in desorbed uranium solution
10,65	10,65	0,0	19,6	19,5	−0,5	—	—	—	—
22,05	22,0	−0,23	2,0	1,98	−1,0	—	—	—	—
1,0	0,985	−1,5	50,0	49,5	−1,0	—	—	—	—
10,05	10,0	−0,5	—	—	—	10,0	0,02	—	—
10,05	10,04	−0,1	—	—	—	0,2	0,0	—	—
10,05	10,25	+1,99	—	—	—	—	—	10,0	0,193
10,05	10,15	+0,9	—	—	—	—	—	4,0	0,046
10,05	10,09	−0,0	—	—	—	—	—	0,2	0,0

containing, on an average, 10-20 mg of uranium taken for analysis, a 5% EDTA-Na solution was added (1-2 ml), and the pH adjusted to 1.7-1.9 while the volume was adjusted to 25-30 ml; the latter was then passed through the cation exchange resin in the sodium form at the rate of 0.8 ml/minute. After washing the column with water (150 ml passed through at the rate of 3.2 ml/minute), the uranium was desorbed with 3 N sulfuric acid, which was passed through at a rate of 1.6 ml/minute. The sulfuric acid solution issuing from the chromatographic column was passed through a bismuth reducer. In this way, desorption and reduction of uranium were realized simultaneously. Uranium was determined by titration with potassium dichromate. The results obtained are given in Table 3; they agree quite satisfactorily with the specified contents.

TABLE 3

Sample	U content, %			Content of other elements, %
	chromatographic method	hydrophosphate method	specified content	
Alloy of U and Mo	91,49	—	91,19	Mo 8,73
	91,24	—	—	—
	91,34	—	—	—
Alloy of U and W	96,103	—	—	—
	96,103	—	96,09	W 3,83
	96,24	—	—	—
	96,24	—	—	—
Concentrate	82,66	82,68	82,58	Contains
	82,66	—	±0,11	Ca, Al, Mn
Uranoso uranic oxide	82,22	—	—	—
	82,04	82,48	—	—
	82,57	—	—	—

The method described for separating uranium from accompanying elements was also tested out on ore materials.

In analyzing uranium ores, the difficulty arises of calculating the amount of EDTA-Na that should be added to mask the other elements. At pH 1.7-1.9 ethylenediaminetetraacetic acid (EDTA) has an insignificant solubility*; accordingly, excess of the uncombined EDTA passes into the precipitate and traps some of the uranium; this was shown spectrographically. Results of uranium determinations were low; for example, for sample 1** (see Table 4), we found 3.07-3.09% of uranium, whereas the true value was 3.33 ± 0.05%. Consequently, the amount of EDTA-Na added to the solution should be such as to prevent precipitation of EDTA.

Depending on the expected uranium content, 0.5-2.0 g of ore was decomposed with hydrochloric acid to

*The solubility of ethylenediaminetetraacetic acid in 0.1 N HCl is 0.16 g/liter, in 0.01 N HCl it is 0.06 g/liter; the determinations were carried out by N.I. Udal'tsova.

**The amount of EDTA-Na added was one-and-a-half times the amount of sample taken.

TABLE 4

Ore No.	U content, %		Ore No.	U content, %	
	chromatographic method	specified content		chromatographic method	specified content
1	3,30	—	2	4,37	4,36±0,02
	3,35	—		4,365	—
	3,26	3,33±0,05		4,25	—
	3,28	—	3	0,120	—
	3,38	—		0,123	0,123±0,002
	3,32	—		0,126	—

which hydrogen peroxide had been added, or with aqua regia and hydrofluoric acid. Excess fluoride ions were removed by a double evaporation with concentrated nitric acid. The hydrochloric or nitric solutions obtained (volume 50 ml) were neutralized with dilute ammonia solution (free from carbonate) until the pH was 1.7-1.9; dry EDTA-Na was added gradually in small portions, and the procedure outlined above for the analysis of uranium-rich products then followed.

Despite the fact that the results obtained (Table 4) are satisfactory, determination of uranium by the given technique has considerable disadvantages; accordingly, the method described cannot be recommended for industrial laboratories.

Separation of Uranium from Accompanying Metals in the Presence of EDTA-Na on a Carboxyl Cation Exchange Resin

a) Ores containing n-0.n% uranium. The compound of uranium with EDTA-Na possesses low stability [15]. The chemisorption character of the absorption of uranium by carboxyl resins suggests the possibility that uranium will be sorbed by these ion exchange resins with destruction of the strongly dissociated complex.

The sorbent used was the carboxyl cation exchange resin Amberlite IRC-50 (10 ml) with a particle size of 0.25 mm.

It was found that at pH 2-8 in the presence of EDTA-Na this cation exchange resin quantitatively sorbed uranium. The pH range 5.5-7.0 was chosen for the separation. As tests showed, V, Mo, W, Fe (III) are not completely sorbed by cation exchange resins under the given conditions.

Ni, Co, Zn, Al, etc., in this pH range, form stable anionic complexes with EDTA-Na [11] and cannot be sorbed by the cation exchange resin.

First of all, the possibility of separating uranium from accompanying elements in the presence of EDTA-Na on a carboxyl cation exchange resin was checked on uranium ores containing whole percentages and tenths of a percent of uranium.

TABLE 5

Ore No.	U content, %		Ore No.	U content, %	
	chromatographic method	specified content		chromatographic method	specified content
3	0,125	0,123+0,001	1	3,28	3,30±0,06
	0,122			3,29	
4	0,613			3,36	
	0,615	0,609+0,004	5	0,212	0,22±0,01
	0,615			0,210	
2	4,33	4,36 ±0,02		0,208	
	4,36				

An aliquot of ore (1-4 g) was decomposed as described above. Into the solution thus obtained (50-75 ml) was added dry EDTA-Na (four times the amount of the aliquot). The pH of the solution was adjusted to 5.5-7.0,

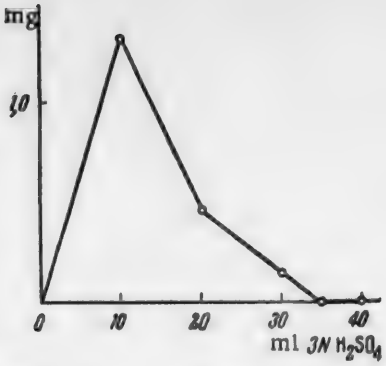

Fig. 5. Desorption curve for 2 mg of uranium with 3 N H_2SO_4 (volume of resin = 2 ml; desorption rate 0.56 cm/minute).

and it was then passed through a column of Amberlite IRC-50 in the sodium form at the rate of 0.8 cm/minute. The subsequent procedure adopted was similar to that used in the case of the sulfonate resin. The results are given in Table 5; the deviation from the specified contents is insignificant.

Other marks of carboxyl resins can be used in the variant just described for the chromatographic separation of uranium from accompanying elements.

b) Ores containing tenths and hundredths of a percent of uranium, and poor solutions from uranium production. Titration with potassium dichromate is not convenient in the case of small amounts of uranium; sorption of uranium is impossible from poor solutions from uranium production, usually soda solutions.

In this connection, we carried out a number of tests, the aim of which was to improve the method suggested earlier, as applied to poor uranium materials.

First of all, it was necessary to find the conditions for separating 0.5-2.0 mg of uranium from accompanying elements. We used a column 28 cm long and 0.6 cm in diameter. The particle size was 0.25 mm, while the rate at which the solution was passed through the column was 0.3 ml/minute; the rate of desorption was 0.6 ml per minute.

It was found that it was sufficient to take 2 ml of sorbent in a swollen state. Under these conditions, it was sufficient to use 35 ml of 3 N sulfuric acid for complete desorption of the uranium. The curve for the desorption of 2 mg of uranium with 3 N H_2SO_4 is shown in Fig. 5.

A series of experiments was carried out on the determination of uranium in synthetic solutions containing various anions, 0.5-2.0 mg of uranium, and 50 mg iron (see Table 6). To the solution was added 0.45 g of EDTA-Na; it was then neutralized with ammonia until the appearance of a red-orange color (pH 5.5-6.5). The separation method was similar to that described above. The uranium was desorbed with 35 ml of 3 N H_2SO_4 and its content determined by titration with ammonium vanadate (0.004 N) (indicator – phenylanthranilic acid).

TABLE 6

Taken, mg		U found, mg	Error, %	Anion	Taken, mg		U found, mg	Error, %	Anion
U	Fe				U	Fe			
0,5	50,0	0,49	—2,0	$SO_4^{''}$	1,0	50,0	1,0	0,0	Cl'
1,0	50,0	0,99	—1,0	$SO_4^{''}$	1,0	50,0	1,0	0,0	NO_3'
1,0	50,0	0,99	—1,0	$SO_4^{''}$	2,0	50,0	2,01	+0,5	NO_3'
1,0	50,0	0,981	—1,9	Cl'	2,0	50,0	1,98	—1,0	$SO_4^{''}$

TABLE 7

Taken, mg				U found, mg	U sorbed, %	Taken, mg				U found, mg	U sorbed, %
U	Fe	P	F			U	Fe	P	F		
1,0	50,0	1,0	—	1,0	100,0	1,0	50,0	—	1,0	1,0	100,0
1,0	50,0	2,0	—	1,0	100,0	1,0	50,0	—	5,0	1,0	100,0
1,0	50,0	3,0	—	0,99	99,0	1,0	50,0	—	10,0	0,99	99,0
1,0	50,0	10,0	—	0,981	98,1	1,0	50,0	—	20,0	0,68	68,0
1,0	50,0	20,0	—	0,867	86,7	1,0	50,0	—	50,0	0,56	56,0
1,0	50,0	50,0	—	0,641	64,1	1,0	50,0	—	100,0	0,37	37,0
1,0	50,0	100,0	—	0,471	47,2						

The mean relative experimental error was found to be within the permissible limits; uranium was completely separated from iron.

The effect of a number of anions on the sorption of uranium from solutions containing EDTA-Na on the cation exchange resin IRC-50 was also studied. The results given in Table 6 indicate that the ions Cl^-, NO_3^-, and SO_4^{2-} do not interfere with the sorption of uranium on the cation exchange resin. Phosphate and fluoride ions, at concentrations ≥10 times that of uranium, lower its sorption (Table 7).

The technique used for analyzing pure uranium ores was identical to that used for the synthetic solutions.* For the analysis of silicate ores it was sufficient to add EDTA-Na in an amount four times that of the aliquot of sample taken; for the analysis of iron ores or ores containing tenths of a percent of calcium, the amount of EDTA-Na taken should be 7-8 times the aliquot of sample. The results are given in Table 8.

TABLE 8

Ore No.	U content, %		Ore No.	U content, %	
	chromatographic method	specified content		chromatographic method	specified content
6	0,069 0,069 0,069 0,069	0,07+0,001	7	0,035 0,035 0,034	0,036 (hydrophosphate method)
5	0,208 0,211 0,213 0,211 0,206	0,22±0,01	8	0,242 0,242 0,244	0,237±0,06
			9	0,313 0,31 0,313	0,325±0,009

In uranium solutions, the main mass of the dry residue is composed of calcium and sodium salts, while the uranium content varies from one to a hundred milligrams per liter. As a result, before effecting separation by a chromatographic method, it is necessary, first of all, to enrich the sample by coprecipitating the uranium on ferric hydroxide. The requisite volume of solution depends on the uranium concentration.

TABLE 9

Solution No.	Content of U, mg				Deviation from the true value, % (relative)
	chromatographic method		ether extraction		
	in the sample	in a liter	in the sample	in a liter	
1	0.72 0.735 0.726 0.726	2.9	0.75	3.0	−3.3
2	1.604 1.604 1.62 1.62	161.2	1.65	165	−2.3

It was found possible to determine uranium in synthetic solution No. 1 (3 mg/liter uranium) and in the soda solution No. 2 (165 mg/liter uranium).

To a sample of solution was added 10 ml of concentrated HNO_3, the solution was boiled for 15 minutes to remove carbon dioxide, and then 1 ml of a 5% solution of $Fe_2(SO_4)_3$ added; the ferric hydroxide was precipitated

*The samples were decomposed in the usual way.

with ammonia solution. The precipitate was filtered off and dissolved on the filter in a hot 1 N acid solution (HNO_3, HCl), 1 g of dry EDTA-Na was added, and the procedure described for the analysis of uranium ores subsequently followed.

The results are given in Table 9.

SUMMARY

Ion-exchange chromatography can be used for separating uranium from accompanying elements, use being made of differences in the capacity of uranium and the other elements to form compounds with EDTA-Na.

Separation is possible in two cases:

in acid media, in which uranium is found in the form of a positively charged ion, most of the accompanying elements form an anionic complex with EDTA-Na and are not sorbed by a cation exchange resin;

in media which are almost neutral, in which uranium is found in the form of an unstable anionic complex, and can be sorbed by carboxyl resins after decomposition of this complex.

Two variants are used depending on the nature and amount of accompanying elements:

removal of uranium from solutions with pH 1.7-1.9 on KU-2 cation exchange resin in the sodium form; this is applicable to materials which are rich in uranium;

removal of uranium from solutions with pH 5-8 on a cation exchange resin of the Amberlite IRC-50 type, in the sodium form; this variant is applicable to both rich uranium ores and to poor ores and poor uranium solutions.

LITERATURE CITED

[1] D.I. Ryabchikov and M.M. Senyavin, Material Presented at the International Conference on the Peaceful Use of Atomic Energy Vol. 8, Geneva, 1955 (Metallurgizdat, Moscow, 1958) p. 328.

[2] D. Dyrssen, Svensk. Kem. Tidskr. 7, 153 (1950).

[3] K. Klement, Z. analyt. Chem. 145, 9 (1955).

[4] K.A. Kraus and F. Nelson, Material Presented at the International Conference on the Peaceful Use of Atomic Energy Vol. 7, Geneva, 1955 (Goskhimizdat, Moscow, 1958) p. 144.

[5] K.A. Kraus, F. Nelson, and G. Moore, J. Am. Chem. Soc. 77, 3979 (1955).

[6] K.A. Kraus, F. Nelson, and G. Moore, J. Am. Chem. Soc. 78, 12, 2692 (1956).

[7] A. Arnfelt, Acta chim. Scand. 9, 9, 1484 (1955).

[8] S. Fisher and R. Kunin, Material Presented at the International Conference on the Peaceful Use of Atomic Energy Vol. 8, Geneva, 1955 (Metallurgizdat, Moscow, 1958) p. 343.

[9] L. Shankar and D. Bkhatnagar, Material Presented at the International Conference on the Peaceful Use of Atomic Energy Vol. 8, Geneva, 1955 (Metallurgizdat, Moscow, 1958) p. 83.

[10] J. Korkisch, Mikrochim. acta 1422 (1956).

[11] R. Přibil, Complexone in Chemical Analysis [Russian translation from Czech] (IL, 1955).

[12] W. Blaedel and A. Knight, Analyt. Chem. 26, 743 (1954).

[13] E.B. Sandell, Colorimetric Determination of Traces of Metals [Russian translation] (Goskhimizdat, Moscow-Leningrad, 1949).

[14] I.M. Kolthoff and J.J. Lingane, Polarography [Russian translation] (Goskhimizdat, Moscow, 1948).

[15] D.I. Ryabchikov, Z.K. Mikhailova, and P.N. Palei, Zhur. Anal. Khim. 14, 581 (1959).*

*Original Russian pagination. See C.B. translation.

[16] K. Macek and R. Přibil, Collection 20, 715 (1955).

[17] P.N. Palei, Material Presented at the International Conference on the Peaceful Use of Atomic Energy Vol. 8, Geneva, 1955 (Metallurgizdat, Moscow, 1958) p. 268.

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NEW METHODS FOR THE DETERMINATION OF VERY SMALL AMOUNTS OF OZONE

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The ever-increasing interest in determining small amounts of ozone is connected with the problems of studying the upper layers of the atmosphere, with the use of ozone as a highly active oxidizing agent in technics, and with the control of the atmosphere in production establishments on account of the appreciable toxicity of ozone. Despite the high reactivity of ozone and despite its reaction with various organic and inorganic materials, there is, as yet, no reliable method for its determination.

We have developed highly sensitive analytical methods which are based on the extinction of fluorescence and on the changes in color of indicator tubes on passing air containing very small amounts of ozone through them.

On the basis of published data on the interaction of ozone with fluorescein and a number of organic dyestuffs, we decided to study the possibility of using them for determination of small amounts of ozone [1-3]. Having established in the first few experiments that when the reaction is carried out in solution it only leads to a negligible effect, in our subsequent work we used solid chemisorbents, finely ground silica gel being impregnated with the appropriate reagents. Of the large number of fluorescent materials that we tested, the most sensitive to ozone were luminol and fluorescein, while, of the organic dyes, the most sensitive was fuchsin. "MSK" silica gel with a particle size ranging from 180 to 250 μ was, first of all, treated with 6 N hydrochloric acid; it was then washed with water until the washings gave no test for chloride ions, and, finally, calcined at 750°; silica gel treated in this way was impregnated with dilute solutions of the reagents indicated.

Preparation of indicator powder based on luminol. 0.025 g of luminol was dissolved in 25 ml of 0.1 N NaOH in a 100-ml standard flask and the volume made up to the mark with distilled water. 1 ml of this solution was transferred into another 100-ml standard flask and diluted with water to the mark. 2.0 ml of this dilute luminol solution was used for impregnating 1 g of silica gel. After careful mixing, the treated silica gel was dried for one hour at 100°.

Preparation of indicator powder based on fluorescein. 0.04 g of fluorescein was dissolved in 1 ml of 10% KOH and the volume made up to 100 ml with water. This solution was diluted 20 times with water to give the solution finally used for impregnating the silica gel; 1 g of silica gel was impregnated with 1.6 ml of the fluorescein solution; it was dried in a drying oven for one hour at 100°.

Preparation of indicator powder based on fuchsin. 0.01 g of fuchsin base was dissolved in 20 ml of alcohol in a 100-ml standard flask and the volume made up to the mark with water. The working solution was prepared by taking 6 ml of the original solution and mixing it with 5 ml of water and 1 ml of 0.01 N HCl. 1.6 ml of this solution was used for impregnating 1 g of silica gel; the silica gel was finally dried at 100° for one hour.

Glass tubes (45 mm long and 2.5 mm in diameter) were packed as tightly as possible with these sorbents; air containing known amounts of ozone was subsequently sucked through these tubes.

In order to prepare gas-air mixtures with low ozone concentrations, individual portions of ozonized air were introduced into evacuated pipets (100-50 ml). The gas mixture was transferred from the pipet into an 8-liter bottle with a ground-glass stopper, a small vacuum having been created beforehand in the bottle. The gas-air mixture was kept for several hours and the ozone content then determined iodometrically [4]. Sampling of test air

TABLE 1

The Relation Between the Length of the Treated Zone of the Indicator and the Amount of Ozone

Luminol			Fluorescein			Fuchsin		
ozone, γ	length, mm	ozone, γ per mm (coefficient)	ozone, γ	length, mm	ozone, γ per mm (coefficient)	ozone, γ	length, mm	ozone, γ per mm (coefficient)
0,8	5	0,16	1,5	5	0,30	1	3	0,33
0,9	6	0,15	1,5	4	0,38	1,75	4,5	0,40
1,1	6	0,18	1,7	5	0,34	1,95	5	0,39
1,27	12	0,11	1,75	5	0,35	2,0	7	0,28
1,6	13	0,12	3,0	9	0,33	2,56	5	0,44
1,7	11	0,15	3,2	9	0,35	3,5	9	0,39
1,75	10	0,17	3,2	10	0,32	4,0	12	0,33
2,2	10,5	0,21	3,4	9	0,38	6,4	15	0,43
3,2	27	0,12	3,5	11	0,32	8,0	19	0,42
	Mean	0,15	6,4	17	0,37	9,6	20	0,48
				Mean	0,34	10	23	0,43
							Mean	0,39

by sucking it through the indicator tubes was carried out while the inlet tube of the bottle was closed. After 0.5 ml of test air had been taken, the vacuum thereby created in the bottle was eliminated by allowing pure air dried by sulfuric acid to pass into it.

After treatment with ozone there is clearly observed in the luminol and fluorescein tubes, when examined under ultraviolet light, a section where the fluorescence has been extinguished, the length of this section being greater the higher the ozone concentration.

In the case of the luminol indicator, the extinction of the bright-blue fluorescence is accompanied by the formation of a dull, greenish color. The fluorescein tubes are decolorized by the action of ozone, and the decolorized part is deprived of its characteristic greenish-yellow fluorescence in the ultraviolet. The reaction of ozone with the fuchsin indicator is expressed by the formation of a blue-violet color – the length of the zone in which the color has changed being again proportional to the amount of ozone.

TABLE 2

Determination of Ozone in the Presence of Nitrogen Oxides

Ozone found, γ/liter	NO_2 found, γ/liter
0.14	1.7
1.5	5.3
1.58	1.0
1.84	5.3
6.5	5.5

The relation between the length of the zone which has reacted and the amount of ozone taken was investigated in a series of experiments using known amounts of ozone. The results obtained are given in Table 1.

On the basis of the results obtained, calculating coefficients (conversion factors) were established for each of the chemisorbents; these conversion factors are expressed in terms of the amount of ozone (γ) corresponding to 1 mm.

As is evident from the table, the luminol indicator is more sensitive than the fluorescein and fuchsin indicators. When luminol tubes are used, 1 mm of extinguished zone corresponds to 0.15 γ of ozone; this is several times more sensitive than all methods of determining ozone hitherto known [5-7].

Remembering that nitrogen oxides always accompany ozone, we studied the effect of nitrogen oxides on the determination of ozone by the indicators recommended [8-10].

Experiments with known concentrations of nitrogen dioxide showed that extinction of fluorescein, just like the change in color of the fuchsin indicator, only occurs when appreciable amounts of NO_2 are used. Of the indicators used, luminol was the least sensitive to nitrogen dioxide. Reaction with this indicator becomes appreciable at about 6 γ, that is, at a concentration 40 times that of the minimum amount of ozone that can be determined.

Fluorescein and fuchsin proved to be more sensitive to nitrogen oxides. In these cases, determination is only possible for amounts of NO_2 which are 13-6 times (respectively) that of ozone.

Ozone is determined as follows. The indicator tubes from which the caps have been removed are connected by one end to a small water or electroaspirator, and 1 liter of air drawn at a uniform rate in the course of 40 minutes through them. The tubes are examined under the light from a PRK-4 lamp and the boundaries of the extinguished zone marked; the length of the zone is then measured in mm in ordinary daylight. Determination of ozone by means of fuchsin tubes is based on the length of the blue-violet zone. In those cases where extinction of fluorescence or the change in color of the indicator has extended through the whole tube (this occurs at high ozone concentrations) the determination should be repeated, a smaller amount of test air being drawn through. Knowing the volume of air sucked through and the length of the zone in the indicator tube where reaction has occurred, the ozone concentration of the test air is calculated using the experimentally established conversion factors.

The methods which we recommend have been used for studying the gaseous composition of the air for various operating conditions of electrofilters designed for trapping dust.

Table 2 contains some results for the determination of ozone in the presence of nitrogen dioxide by means of luminol indicator tubes.

SUMMARY

Highly sensitive quantitative methods have been developed for the determination of ozone which are based on extinction of the luminescence of luminol and fluorescein.

A linear colorimetric method has been developed for determining ozone which is based on the change in color of silica gel impregnated with fuchsin solution.

It has been established that ozone can be determined in the presence of appreciable amounts of nitrogen oxides.

Of the indicators suggested, the one which is most sensitive to ozone, and least sensitive to nitrogen oxides, is an indicator based on luminol.

LITERATURE CITED

[1] M.S. Egorov, Profilakt. Meditsina 4, 1 (1928).

[2] M.S. Egorov, Gigiena, Bezopasnost' i Patologiya Truda 7, 46 (1930).

[3] Z.A. Chavchavadze and I.I. Kaliashvili, Gigiena, Bezopasnost' i Patologiya Truda 10, 44 (1929).

[4] M.A. Petrova and A.K. Yakovtsevskaya, Trudy Vses. Nauchno-Issledovatel'skovo Instituta Okhrany Truda, Leningrad 7, 8, 94 (1934).

[5] M. Konstantinova-Shlezinger, Trudy Fizicheskovo Instituta AN SSSR 1, 1, 119 (1939).

[6] B.L. Crabtree and R.H. Ericson, India Rubber Weekly 125, 719 (1952).

[7] W. Deckert, Z. analyt. chem. 153, 189 (1957).

[8] G.A. Gorodetskii, Zhur. Priklad. Khim. 9, 353 (1936).

[9] G.A. Gorodetskii, Zhur. Priklad. Khim. 12, 1637 (1939).

[10] Olga Tanaevsky and Arlette Vassy, C. r. Acad. Sci. 244, 7, 924 (1957).

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RAPID METHODS OF MICROELEMENTAL ANALYSIS

COMMUNICATION 17. SIMULTANEOUS MICRODETERMINATION OF CARBON, HYDROGEN, MERCURY, AND HALOGEN ON ONE ALIQUOT OF ORGANIC MATERIAL*

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Methods for the gravimetric determination of carbon, hydrogen, and mercury based on a combination of elemental analysis with weighing of the mercury as a gold amalgam [1, 2] are inadequate and are, accordingly, not used.

Absorption of mercury by gold foil or wire, during decomposition of organic materials, has been used for its quantitative microdetermination by Boetius [3] and Korshun and Lavrovskaya [4]. We have used the rapid method of microdetermination of carbon and hydrogen in compounds described by Korshun and Klimova [5-8], the mercury being trapped by gold, so that these elements are determined simultaneously; the technique for combustion in a special case developed earlier was used for this purpose [9].

TABLE 1

Expt. No.	Weight of case + gold, mg*		
	before expt.	after passing 600 ml O_2 through	change in weight
1	4.840	4.828	−0.012
2	3.478	3.492	+0.014
3	3.800	3.790	−0.010
4	1.030	1.026	−0.004
5	8.750	8.730	−0.020

*The readings of the rider and the microscale are given without taking into account the tare.

The method consists essentially of subjecting an aliquot of material to rapid pyrolytic combustion, while the mercury is kept back in a quartz case containing gold, the case being located inside the combustion tube; the amount of mercury is determined by the change in weight of this case plus its contents. Carbon and hydrogen are determined as usual [5-8]. The same quantity of gold can be used for a long time, since it is readily freed from mercury as the latter accumulates by simply heating it in an air stream. During blank runs, and during combustion of materials not containing mercury, the weight of the case plus gold remains constant within the limits ±0.010-0.020 mg (Table 1); this ensures that mercury can be determined with an accuracy of 0.6-0.7% absolute.

If halogen is present at the same time, it too can be determined simultaneously with C, H, and Hg. For

*Communication 16, see Zhur. Anal. Khim. 14, 123 (1959). See C.B. translation.

**Deceased.

this purpose the products of pyrolytic combustion, after issuing from the test tube, pass first over heated silver in order to absorb the halogen and then over cooled gold, which traps the mercury.

In the same way, it is possible to determine sulfur, as long as the test material does not contain halogen as well as sulfur [10, 11]. Results for the simultaneous determination of C, H, and Hg, and also of C, H, Hg, and halogen or sulfur are given in Table 2.

TABLE 2*

Test material	Hg, %		C, %		H, %		Halogen and sulfur, %	
	found	dif.	found	dif.	found	dif.	found	dif.
$C_{11}H_{12}HgO$								
2-Methyl-4-phenylmercurbutine-3-ol-2	55,89	+0,29	36,86	+0,25	3,37	+0,02		
C—36,61%; H—3,35%; Hg—55,60%	55,63	+0,06	36,65	+0,04	3,34	—0,01		
$C_{18}H_{18}Hg$								
Bis-(bicyclo[2,2,1]heptene-3-yl-ethinyl)-mercury	45,77;	—0,36	49,56	—0,15	4,14	—0,03		
C—49,71; H—4,17; Hg—46,13%	46,65;	+0,48	49,63	—0,08	4,28	+0,11		
$C_3H_3Cl_3Hg$								
γ,γ'-dichlorallylmercury chloride	58,02;	+0,05	10,47	+0,06	1,00	+0,13	30,74	0,00
C 10,41%; H—0,87%; Cl—30,74%;								
Hg—57,97;	57,67	—0,30	10,54	+0,013	0,96	+0,09	30,84	+0,10
$C_{14}H_{14}Hg_4$								
Tropilium mercurtetraiodide	22,60	+0,07	18,68	—0,20	1,55	—0,03	56,97	—0,04
C—18,88%; H—1,58%; J_4—57,01%;								
Hg—22,53%	22,34	—0,19	18,80	—0,08	1,56	—0,02	57,38	+0,37
$C_{20}H_{18}Br_2HgN_4$								
Dimethylaminophenylmercur-4,4'-dibromdiazoaminobenzene	29,73	0	35,71	+0,12	2,68	—0,01	23,80	+0,12
C—35,59%; H—2,69%; Hg—29,73%;								
Br—23,68%	30,03	+0,33	35,58	—0,01	2,72	+0,03	23,61	—0,07
$C_{18}H_{16}HgN_2O_2$								
Dimethylaminophenylmercur-4-nitrosonaphthol-1	40,46	—0,24	44,09	+0,24	3,27	0		
C—43,85%; H—3,27%; Hg—40 70%	40,83	+0,13	43,97	+0,12	3,31	+0,04		
$C_{22}H_{20}HgN_2O_2$								
Dimethylaminophenylmercur-α-benzylmonooxime	36,40;	—0,41	48,39;	—0,09	3,84	+0,14		
C—48,48%; H—3,70%; Hg—36,81%	36,36	—0,45	48,53	+0,05	3,83	+0,13		
$C_{20}H_{18}BrHgN_5O_2$								
Dimethylaminophenylmercur-4-bromo-4-nitrodiazoaminobenzene	31,72	+0,42	37,78	+0,30	2,99	+0,16		
C—37,48%; H—2,83; Hg—31,30%;								
Br—12,47%	31,52	+0,22	37,61	+0,13	2,82	—0,01		
$C_{22}H_{23}Hg_2N_3O_2S$								
Bis-dimethylaminophenylmercur-benzosulfamide	50,30	0,00	33,43	+0,23	3,11	—0,03	4,12	+0,09
	50,10	—0,20	33,33	+0,13	3,03	—0,11	4,09	+0,06
C—33,20%; H—3,14%								
Hg—50,30%; S—4,03%								
$C_{14}H_8Br_8Fe_2Hg_5O_4$								
The mercury derivative of cyclopentadienyl iron**	50,32	—0,02	8,44	0	0,59	+0,27	31,81	—0,29
C—8,44%; H—0,32%; Br—32,10%;								
Fe—5,61%; Hg—50,34%	50,14	—0,20	8,33	—0,11	0,58	+0,26	32,22	+0,12

*All the analyses given in Table 2 were carried out with aliquots of 5-8 mg.

**5.46 and 5.40% Fe were simultaneously found in the same aliquots.

These examples do not exhaust the possibilities of simultaneous determination of mercury and other elements in organic compounds. For example, it might be expected that the various metals which are weighed in the form of their oxides could be simultaneously determined with carbon, hydrogen, and mercury, and sometimes even with halogen on the basis of the residue left after combustion of one aliquot. As an example, one can cite the analysis of the mercury derivative of iron cyclopentadiene, in which carbon, hydrogen, mercury, iron, and halogen were determined on one aliquot (Table 2).

It is particularly interesting to dwell further on the analysis of materials containing nitrogen. According to the observations of Boetius [3], during combustion of materials containing mercury and nitrogen in oxygen, high results are obtained for mercury as the result of the formation of a certain amount of mercury nitrate from the interaction of nitrogen oxides and mercury. Accordingly, Boetius recommends that combustion of nitrogen-containing materials be carried out in a current of an inert gas and that the nitrogen oxides be reduced with metallic copper inside the combustion tube. Boetius' method, like the modification of Korshun and Lavrovskaya [4], was developed on the basis of the principles of Pregl's classical microanalysis, with slow evaporation of the aliquot and quantitative oxidation of the vapors of the material by means of the oxidizing packing of the combustion tube. It is known that, under these conditions, the presence of nitrogen in the test material is conducive to the formation of appreciable amounts of nitrogen oxides [12, 13], trapping of which is absolutely essential in order to get

TABLE 3

Expt. No.	Weight of case plus gold, mg*			Notes
	before combustion	after combustion	difference	
1	7.660	7.672	+0.012	5-6 mg lots of picric acid were burnt. The case contained 7-11 mg of mercury.
2	1.991	1.972	−0.019	
3	1.951	1.963	+0.012	
4	1.963	1.959	−0.004	

*The readings of the rider and the microscale are given without taking into account the tare.

correct results for the elemental analysis. It is otherwise in the case of rapid pyrolytic combustion, where the yield of nitrogen oxides, even during analysis of nitro compounds, does not exceed 12-14% of the total amount of nitrogen [7, 2]. In order to establish whether or not mercury nitrate is formed under the conditions used for rapid pyrolytic combustion of nitrogen-containing compounds, we carried out a series of combustions of picric acid in which a case containing gold, in which the mercury was found both in the form of an amalgam and as a film on the walls of the case, was placed inside the combustion tube. The change in the weight of the case after the experiments did not exceed the usual errors in weighing (Table 3). After these experiments, the case was washed several times with water, and the wash liquor tested for any nitrate ions by the reaction with diphenylamine. No nitrate ions were detected. Thus, we concluded that under our conditions no mercury nitrate is formed. Determinations of carbon, hydrogen, mercury, and halogen in materials containing nitrogen in the oxidized form confirm this conclusion (Table 2).

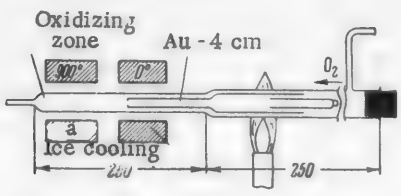

Fig. 1. Tube for determination of carbon, hydrogen, and mercury.
Key: (a) = MAG - 6R.

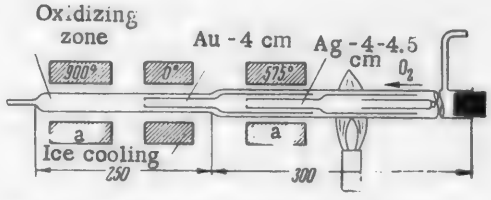

Fig. 2. Tube for determination of carbon, hydrogen, mercury, and halogen (or sulfur).
Key: (a) = MAG - 6R.

Apparatus. The apparatus is the same as that used for the simultaneous determination of C, H, and halogen in a case [9]. The arrangement of the case plus gold, the sample, and oxidizing zone is shown in Fig. 1. When the test material contains halogen, another case containing silver is also introduced into the combustion tube, as shown in Fig. 2. In this instance, the length of the wide part of the combustion tube should be not less than 30 cm. For rapid cooling of the absorption apparatus and of the case, we use in our laboratory metallic blocks with indentations corresponding in size to the Pregl apparatus and the case (Figs. 3 and 4).

Reagents. Thin gold wire or foil is used for trapping the mercury. Halogen is trapped with silver metal in the form of a mesh, foil, or wire weighing about 3 g. Silvered pumice cannot be used in this case because it traps part of the mercury and the results obtained for mercury and halogen are incorrect. The other reagents are are the same as those used for the determination of carbon and hydrogen [5-11].

Analytical procedure. We shall only deal with the techniques connected with determination of mercury and the positioning of the case and the test tube in the combustion tube, since that part of the method dealing with the determination of carbon, hydrogen, and halogen remains unchanged [9].

Before using a case, it is boiled in 1:1 HCl for ten minutes; it is then washed, dried, and finally calcined in the combustion tube. A layer of gold 4-cm long is placed in the calcined case (in its narrow part). The gold should be packed loosely so that it does not offer any resistance to the gas flow. The case plus gold are weighed, using a tared flask containing lumps of glass. Before starting an analysis, a blank test is run in which the case is placed in the combustion tube as shown in Fig. 1. Should the case already contain mercury absorbed during previous runs, then during the blank, as well as during combustion, the gold layer must be cooled with ice so that

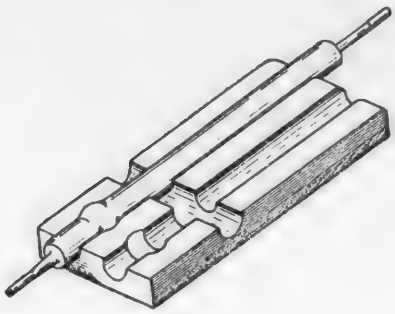

Fig. 3. Metal block for cooling the absorption apparatus.

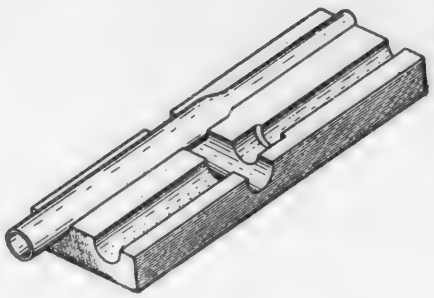

Fig. 4. Metal block for cooling the case.

very small particles of mercury are not carried outside the limits of the case by the stream of hot oxygen issuing from the heated combustion tube. During the combustion of mercury-containing compounds, the case together with the small tube containing the sample (5-8 mg), is moved into the combustion tube to a distance of not less than 5 cm from the oxidizing zone, the oxygen throughput is adjusted to 30-35 ml/minute, and combustion of the test material is commenced with a gas burner. When combustion is complete, the wide part of the case is calcined with the burner. The narrow part should not be heated, so as to avoid evaporation of the mercury which has accumulated there. It should be noted that the mercury only partially falls onto the gold. Part of it settles on the cold walls of the narrow part of the case in the form of a very fine grey layer. When combustion has finished, the burner is extinguished and the cooling stopped, while the oxygen continues to pass for ten minutes through the combustion tube. During this period the aliquot for the next determination is taken. The absorption apparatus is disconnected and the tube immediately sealed with a stopper. The case is withdrawn and the tube removed from it, the case is transferred to the balance room and placed on the metal block near the balance (Fig. 4); it is weighed 25 minutes after removing it from the combustion tube [9].

When the test material contains halogen, it is necessary to introduce one more quartz case packed in its narrow section with metallic silver (see Fig. 2) into the combustion tube. When the wide part of the combustion tube is 30 cm in length, then both cases are freely arranged and combustion proceeds sufficiently far from the rubber stopper. It is of particular importance to ensure that all the silver layer is heated to 575° and that the mercury cannot be held back on the colder ends of the layer in the form of a silver amalgam. Combustion is carried out as described above. When combustion is complete, the burner is extinguished, the oven in which the silver is located is removed, and oxygen passed through for a further ten minutes; for the first five minutes, the cooling is continued, while for the second five minutes, the ice is removed. The cases containing the silver and gold are weighed, 25 and 30 minutes, respectively, after their removal from the combustion tubes.

It is recommended that the gold be regenerated at the end of each working day. For this purpose, the case is placed in a clean quartz tube with drawn-out ends, the tube is connected through a small washer filled with 1:1 nitric acid, to a Mariotte flask or to a water pump, and air is sucked through the tube while the gold is heated with a burner or an oven. When all the mercury has been driven off the surface of the gold, and, accordingly, from the case, the latter is removed and the tube washed with nitric acid.

SUMMARY

A method has been developed for the simultaneous microdetermination of carbon, hydrogen, mercury, and halogen in organic compounds; it is based on the pyrolytic combustion of the organic material, and the gravimetric determination of the four elements. Carbon, hydrogen, and halogen are determined by a method described earlier, while the mercury is trapped in the combustion tube in a special case filled with gold, and is then determined from the increase in weight of the case. The deviation of the experimental results obtained for mercury from the theoretical values does not exceed 0.6-0.7% absolute.

It has been shown that it is possible to determine mercury in materials containing nitrogen, and it has been demonstrated that, under pyrolytic combustion conditions, no mercury nitrate is formed.

It has been shown that when a test material contains a heavy metal which does not give volatile salts with a halogen, the metal can be determined simultaneously with carbon, hydrogen, mercury, and halogen.

LITERATURE CITED

[1] E. Frankland and B.F. Duppa, Ann. 130, 107 (1864).

[2] A. Abelmann, Berichte 47, 2935 (1914).

[3] M. Böetius, J. prakt. Chem. N.F. 151, 9-12, 279 (1938).

[4] M.O. Korshun and E.V. Lavrovskaya, Zhur. Anal. Khim. 3, 322 (1948).

[5] M.O. Korshun and V.A. Klimova, Zhur. Anal. Khim. 2, 274 (1947).

[6] M.O. Korshun and V.A. Klimova, Zhur. Anal. Khim. 3, 176 (1948).

[7] M.O. Korshun and V.A. Klimova, Zhur. Anal. Khim. 4, 292 (1949).

[8] M.O. Korshun and N.É. Gel'man, New Methods of Elemental Microanalysis [in Russian] (Goskhimizdat, Moscow-Leningrad, 1949).

[9] M.O. Korshun, N.É. Gel'man, and N.S. Sheveleva, Zhur. Anal. Khim. 13, 695 (1958).*

[10] M.O. Korshun, Zhur. Anal. Khim. 7, 101 (1952).*

[11] M.O. Korshun and N.S. Sheveleva, Zhur. Anal. Khim. 7, 104 (1952).*

[12] A. Friedrich, Mikrochem. 23, 129 (1937).

[13] A.E. Heron, Analyst 72, 142 (1947).

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SEPARATION OF THE LOWER ALIPHATIC ALCOHOLS BY MEANS OF PAPER CHROMATOGRAPHY AND THEIR QUANTITATIVE DETERMINATION

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The problem which confronted us was to develop a method for separating mixtures of the lower aliphatic alcohols (methyl, ethyl, n-propyl, and n-butyl) which would be applicable to the analysis of the oxidation products of butane under conditions approximating critical conditions (temperature 145°, pressure 50 atmos.[1]). Quantitative separation and determination of alcohols is realized, in the main, by the method of separate oxidation of the alcohols in solutions freed beforehand from other oxidation products [2], while the difference in the solubilities of the alcohols in the aqueous and organic layer at various pressures is also used [3-6]. The drawbacks of these methods are the difficulties involved in carrying them out, the low experimental accuracy, and the impossibility of working with small amounts of materials.

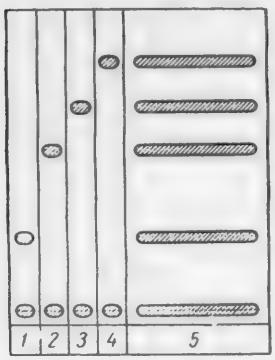


Fig. 1. Chromatogram of the 3,5-dinitrobenzoates of the lower aliphatic alcohols and their mixtures on acetylated paper. Mobile phase – heptane; stationary phase – methanol; t = 20°: 1) methanol; 2) ethanol; 3) n-propanol; 4) n-butanol; 5) mixtures of all four alcohols. The 3,5-dinitrobenzoic acid remains on the line on which the spots were placed originally.

The chromatographic separation of alcohol derivatives on silica gel [7-9] is complicated to carry out and is of low efficiency. Considerably more promising is the separation of the aliphatic alcohols by means of adsorption and partition chromatography on paper of their 3,5-dinitrobenzoic esters [10-12], 3,6-dinitrophthalates [13], alkylhydrophthalates [14-15], and also of their xanthogenates [16-18].

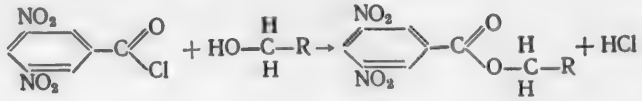
The 3,5-dinitrobenzoates of the alcohols yield the most reliable results. Other alcohol derivatives either demand preliminary careful purification of the test solution from organic compounds present in them, or the R_f values for the homologous series of alcohols differ too little from each other.

All published methods on the separation of alcohols by means of paper chromatography give only qualitative indications of the composition. We have developed a technique for the quantitative determination of aliphatic alcohols by this method. One of the basic difficulties which arises during development of a quantitative method is to achieve a constant, equal, and readily reproducible yield of the esters for all the alcohols. It is also necessary to choose conditions for the quantitative, selective determination of the isolated derivatives.

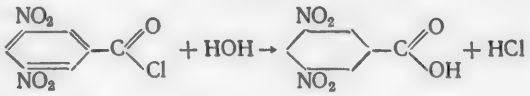
The method of isolating the 3,5-dinitrobenzoates from an anhydrous hydrocarbon medium [19, 20] required modification in order to apply it to the oxidation products of condensed butane, since the mixture contains a considerable amount of water (10-15%). Removal of moisture by extraction or by drying is impossible in the given instance, since this would lead to a large loss of alcohols.

The method used for preparing and isolating the 3,5-dinitrobenzoates was developed on the basis of synthetic mixtures of alcohols in a medium containing 15-20% of water and 80-85% hexane (or heptane).

To the mixture of alcohols was added 0.5 ml of pyridine and a saturated benzene solution of 3,5-dinitrobenzoylchloride. The amount of the latter added was determined on the basis that, in addition to the main reaction which leads to the formation of the ester:



there also occurs the side reaction,



leading to additional expenditure of 3,5-dinitrobenzoylchloride.

In order to ensure that the reaction goes to completion, the mixture was kept at 50-60° for 10-15 minutes in a round-bottomed flask fitted with a reflux condenser.

The reaction products partly dissolved and partly settled out as a precipitate. The reaction liquid was then poured into a measuring cylinder, while the precipitate remaining was washed with small portions of ether into the same measuring cylinder; the level of the latter was adjusted to 120 ml.

After all these operations, the test liquid contained some 3,5-dinitrobenzoylchloride and 3,5-dinitrobenzoic acid formed by hydrolysis of the latter in addition to the oxidation products, pyridine, and the 3,5-dinitrobenzoates of the alcohols. The method of washing the test solution free from 3,5-dinitrobenzoylchloride and 3,5-dinitrobenzoic acid by means of 1 N alkali solution [8] is not suitable for a quantitative method, since the loss of the 3,5-dinitrobenzoates that thereby occurs amounts to 20-25%. However, it is possible, in general, to avoid purification of the 3,5-dinitrobenzoates of the alcohols, and to use the reaction liquid directly for quantitative chromatography. The reason for this is that most of the chromatogram developers recommended in the literature

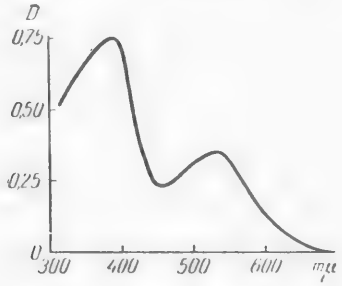


Fig. 2. Absorption curve of the 3,5-dinitrobenzoates of aliphatic alcohols.

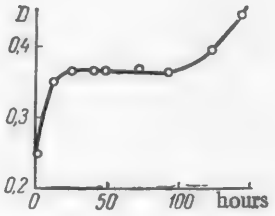


Fig. 3. Optical density of standard chromatograms of the 3,5-dinitrobenzoates treated with Yanovskii reagent stored for varying periods.

for systems similar to ours only record materials containing a benzene ring with the two nitro groups in the meta position. Accordingly, under our conditions, only 3,5-dinitrobenzoylchloride and 3,5-dinitrobenzoic acid can interfere. Hydrolysis of 3,5-dinitrobenzoylchloride to the acid, on placing the solution on the paper and drying the spot, proceeds almost to completion. Thus, the only product which can interfere with the determination is 3,5-dinitrobenzoic acid. The latter remains on the paper on the spot where it is first placed (R_f = 0), consequently, for the quantitative determination of alcohols, it is possible to use a solution of their benzoates without any preliminary purification of these benzoates from the original reagents and other reaction products. The chromatograms were run on special paper type "Leningradskaya," this paper being acetylated beforehand [21, 22].

Absolute methanol was used as the stationary phase and hexane, heptane, or nonane as the mobile phase.

Ascending and descending chromatography gave equal results. In most experiments, ascending chromatograms were run, since the experimental technique involved is simpler.

The solution containing the 3,5-dinitrobenzoates of the alcohols was placed on acetylated paper 120 x 130 mm, in a thin band at a distance of 20 mm from the edge of the paper; the paper was then dried and placed in a chromatographic cell. The method of separation is described in the literature [10]. Good resolution of the bands was achieved on using 10^{-7} g-mole of the 3,5-dinitrobenzoates; larger amounts led to overloading of the paper, and resolution is not so good.

TABLE 1

R_f Values for the 3,5-Dinitrobenzoates of the Alcohols on Different Samples of Acetylated Paper

Batch No. of paper	Mobile phase	R_f (t = 20°, l = 280 mm)			
		methanol	ethanol	propanol	n-butanol
I	Hexane	0.46	0.61	0.68	0.77
I	Heptane	0.36	0.50	0.63	0.67
I	"	0.32	0.50	0.61	0.71
I	"	0.32	0.54	0.60	0.72
I	Nonane	0.22	0.32	0.43	0.54
II	"	0.14	0.30	0.41	0.51
II	Heptane	0.19	0.33	0.44	0.52
II	Hexane	0.26	0.36	0.49	0.62
III	"	0.25	0.36	0.43	0.52
IV	Heptane	0.33	0.54	0.72	0.84

The developer used was Yanovskii reagent (4 g NaOH + 200 ml methanol + 400 ml acetone) which gives a blue-violet color when the solution contains compounds with two nitro groups in the meta position. This reagent has decided advantages over other developers,such as rhodamine Zh [10], alcoholic alkali [11], α-naphthylamine solution [23], stannous chloride in concentrated HCl with subsequent formation of azomethine compounds, etc., since formation of the colored compound is quantitative and the color obtained is fairly stable.

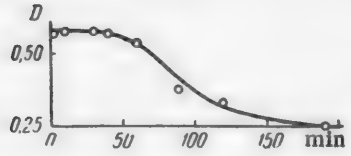


Fig. 4. Change in optical density of 3,5-dinitrobenzoates with time, after spraying them with Yanovskii reagent.

Qualitative detection of the alcohols. The arrangement of the alcohol derivatives on the chromatographic paper after development is shown in Fig. 1. The band of the 3,5-dinitrobenzoic acid remains at the spot on the paper where the solution was originally placed; there follows (from bottom to top) the bands for the 3,5-dinitrobenzoates of methanol, ethanol, n-propanol, and n-butanol. R_f values for the 3,5-dinitrobenzoates of the alcohols we are interested in have been given in [10]; they are: methanol 0.24, ethanol 0.39, n-propanol 0.46, and n-butanol 0.57. However, R_f values are not strictly constant values, and depend to a very considerable extent on the type of paper used. The R_f values found in the present work for different samples of acetylated paper are given in Table 1.

As these results show, there is a good agreement between the R_f values for one batch of paper, but when the paper is changed, the differences become significant. Because of this, a control spot of the 3,5-dinitrobenzoate of one of the alcohols is placed on each chromatogram alongside the band of a test mixture; this excludes the possibility of errors connected with variability in the R_f values.

Quantitative determination of alcohols. The individual 3,5-dinitrobenzoates of the alcohols isolated from their mixtures were determined on the basis of the absorption of the light by the colored compound formed on spraying the chromatograms with Yanovskii's reagent.

After development, the spots were cut out, treated with 20-ml methanol,and the optical density measured on a SF-4 spectrophotometer. The absorption curve of the compound formed is shown in Fig. 2. It has two absorption maxima at 385 and 535 mμ. Series measurements were carried out at 385 mμ.

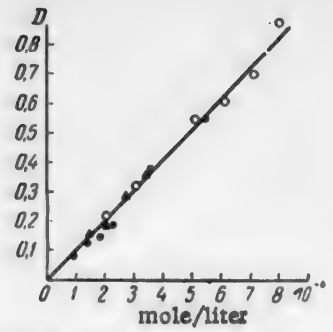


Fig. 5. Calibration curve: o) methanol; ▲) ethanol; ●) butanol.

Freshly prepared Yanovskii reagent is not suitable for quantitative determinations; the compound formed on development of a chromatogram has a lower optical density than the density obtained under the same conditions but using a reagent which has been allowed to stand for some time. The use of Yanovskii reagent which has been stored for a long time gives considerably higher optical densities as a result of the darkening of the reagent itself. As can be seen from Fig. 3, Yanovskii reagent, used after being stored for 24 hours, gives readily reproducible results in the course of the next 70-75 hours.

The colored compound formed on spraying is also unstable. However, as can be seen from Fig. 4, the optical density hardly changes at all 45 minutes after spraying. This time is quite sufficient for measurements.

The quantitative content of the alcohols was established on the basis

TABLE 2

Separation and Quantitative Determination of Normal Aliphatic Alcohols from Their Mixtures in Aqueous-Hydrocarbon Media

Alcohol, mole·10^6		Found, mole·10^6		
		Expt. 1	Expt. 2	Expt. 3
Methanol	8.24	8.40	8.20	8.50
Ethanol	5.60	5.35	5.70	5.52
Propanol	4.40	4.28	4.35	4.35
Butanol	3.58	3.52	3.54	3.50

TABLE 3

Quantitative Determination of Alcohols in Pure Heptane and in Heptane Containing 20% H_2O

Alcohol	Alcohol concentration (mole/liter)	D			
		heptane		0% C_7H_{16}+ +20% H_2O	
		1	2	3	4
Butanol	$2,24 \cdot 10^{-4}$	0,212	0,215	0,210	0,210
"	$5,37 \cdot 10^{-4}$	0,540	0,520	0,500	0,520
Propanol	$3,35 \cdot 10^{-4}$	0,340	0,340	0,350	0,328
Ethanol	$2,14 \cdot 10^{-4}$	0,220	0,210	0,180	0,210
"	$3,52 \cdot 10^{-4}$	0,330	0,350	0,360	0,345
Methanol	$7,21 \cdot 10^{-4}$	0,720	0,715	0,710	—
"	$8,24 \cdot 10^{-4}$	0,840	0,865	0,825	0,850

of the optical density of the solutions using a special calibration curve. Such calibration curves were constructed for methanol, ethanol, and butanol for concentrations of $2 \cdot 10^{-4}$ to $8 \cdot 10^{-4}$ m/liter (Fig. 5). The optical density of the solutions obtained is directly proportional to the concentration of the alcohol and is the same for all three alcohols.

The proportionality between the optical density and alcohol concentration (within the limits 10^{-4} to 10^{-3} M/liter) shows that the yield of the alcohol derivatives, during all the stages of treatment, either approximates to 100%, or, even though it changes, is strictly proportional to the original concentration of the alcohol.

The method gives fully satisfactory results (Table 2); the experimental accuracy is equal to 1.5%.

In order to establish the possibility of using the suggested method for determining alcohols in hydrocarbon-

water medium, and in a hydrocarbon medium, a series of experiments were made on synthetic mixtures. As is evident from Table 3, the yield of the esterified products is the same in all cases within the limits of experimental error. This means that water present in amounts up to 20% in the test solutions does not interfere.

The author wishes to thank N.M. Émanuél and Z.K. Maizus for their valuable advice in carrying out this work.

SUMMARY

A method has been developed for the chromatographic separation and quantitative determination of methanol, ethanol, propanol, and butanol in the form of the corresponding esters of 3,5-dinitrobenzoic acid. Quantitative determination of the alcohols is possible in the presence of water and other oxidation products of the hydrocarbon (butane).

LITERATURE CITED

[1] N.M. Émanuél, Doklady Akad. Nauk SSSR 110, 245 (1956).*

[2] D.M. Newitt and L.S. Thornes, J. Chem. Soc. 1656 (1937).

[3] D.M. Newitt and W.G. Schmidt, J. Chem. Soc. 1665 (1937).

[4] P.N. Pease and W.P. Minro, J. Am. Chem. Soc. 56, 2034 (1934).

[5] D.M. Newitt and P. Szego, Proc. Roy. Soc. A 147, 555 (1934).

[6] W.A. Bone and S.G. Hill, Proc. Roy. Soc. A 129, 434 (1930).

[7] E.M. Brumberg, Transactions of the All-Union Conference on Chromatography [in Russian] (Izd. AN SSSR, Moscow, 1952).

[8] A.F. Lukovnikov, Transactions of the Commission on Anal. Chem. Acad. Sci. USSR, vol. VI (1955) p. 191.

[9] A.D. Holley and R.W. Holley, Analyt. Chem. 24, 216 (1952).

[10] D.F. Deigh, Nature 169, 706 (1952).

[11] R.G. Rice, D.J. Keller, and J.G. Kirchner, Analyt. Chem. 23, 194 (1951).

[12] J.W. White and E.C. Dryden, Analyt. Chem. 20, 853 (1948).

[13] T. Momose and A. Yamada, J. Pharm. Soc. Japan 71, 980 (1951).

[14] P.E. Henze, Analyt. Chem. 27, 1349 (1955).

[15] P.Y. Elving and U.B. Warskowsky, Analyt. Chem. 19, 1006 (1947).

[16] T. Kariyone and Y. Hashimoto, Nature 168, 511 (1951).

[17] Y.W. Spanyer and Y.P. Phillips, Analyt. Chem. 28, 253 (1956).

[18] T. Kariyone, Y. Hashimoto, and M. Kimura, J. Pharm. Soc. Japan 73, 1093 (1953).

[19] V.S. Johnson, R.D. Shennam, and R.A. Reid, Organic Reagents for Organic Analysis [Russian translation] (IL, Moscow, 1948).

[20] S. Vaibel', Identification of Organic Compounds [Russian translation] (IL, Moscow, 1957) p. 71.

[21] M.B. Neiman, A.F. Lukovnikov, and V.N. Levkovskii, Doklady Akad. Nauk SSSR 81, 841 (1951).

[22] V.L. Pikaeva, Zhur. Anal. Khim. 14, 184 (1959).*

[23] T.W. Reichstein, Helv. chim. acta 9, 799 (1926).

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ANALYSIS OF MIXTURES OF ANILINE, MONO- AND DIMETHYLANILINE

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The analysis of mixtures of primary, secondary, and tertiary aromatic amines has been described in a large number of general textbooks and original papers [1-7]. In recent years, for nonaqueous mixtures of amines, new methods, mainly acidimetric, have been developed [8-11]. For the analysis of aqueous solutions of aromatic amines, we turned our attention to methods widely used in aniline-dye plants, according to which the total content of aniline and monoalkylaniline are determined on the basis of the nitrite used up in diazotization and nitration of the sample in the presence of Br^- ions, while the aniline content is determined separately by coupling the diazotized sample with a solution of β-naphthol added from a buret [12], or with a measured amount of R-salt, excess of which is titrated with a solution of p-tolyldiazonium chloride [13].

During a check on mixtures of pure aniline, monomethylaniline, and dimethylaniline, it was found that the accuracy of aniline determination by azo coupling is considerably less than the accuracy possible by diazotization. The errors in the determination of aniline and monomethylaniline, and also the high degree of skill required on the part of the analyst carrying out the azo coupling, led us to check on the acidimetric method of analysis in aqueous solutions.

Hantzsch [14] pointed out the strong basic properties of phenyldiazonium hydroxide long ago.

Cherkasskii [15] and Rostovtsev [16] later carried out potentiometric studies of solutions of diazonium chlorides and the completeness of the hydrolysis of these salts. Grachev [17] in a number of papers also made a potentiometric study of the structure and conversion of diazo compounds. The dissociation constant of phenyldiazonium hydroxide is equal to $10^{-3.1}$ according to I.V. Grachev (according to Hantzsch it is $10^{-2.9}$). A 0.5 N solution of phenyldiazonium chloride has a pH of 5.6. Bearing in mind that conversion of diazo solutions only occurs at higher pH values, one might expect a high degree of accuracy on titrating excess acid with alkali to the equivalence point of phenyldiazonium chloride.

During diazotization, one mole of aniline hydrochloride reacts with one mole of nitrite and one mole of hydrochloric acid to form phenyldiazonium chloride. Under the same conditions, nitrosation of monomethylaniline hydrochloride proceeds without additional expenditure of acid. Dimethylaniline hydrochloride, at not very high concentrations, hardly changes at all under the conditions used for analytical diazotization.

From the amount of acid which enters into the reaction during diazotization, it is possible to determine the amount of primary amine; while from the amount of nitrite used up, it is possible to determine total primary and secondary amines, and from the amount of acid used to combine with the amines up to the equivalence point, it is possible to determine the sum of all three amines.

Such an acidimetric determination of primary amine in a mixture of amines has not hitherto been used as an analytical method.

Analytical procedure. 1. Determination of the total amount of acid used for neutralizing the amines and excess acid. 20-30 g of the mixture of amines is dissolved in a 500-ml standard flask in 200 or 250 ml of 1 N hydrochloric acid; the solution is diluted with water to the mark. Let the amount of 1 N HCl used be N ml.

2. Determination of excess acid. To 50 ml of test solution is added 15 drops of a 0.1% solution of tropeoline 00, and the solution then titrated with 0.5 N NaOH using a reference solution (the pH of the solution is adjusted to

Analysis of Mixtures of Known Composition

Components	Composition, % wt.	Found, % wt.
Aniline	8.72	8.45
Monomethylaniline	79.48	79.7
Dimethylaniline	11.8	11.85
Aniline	8.72	9.5
Monomethylaniline	79.48	78.5
Dimethylaniline	11.8	11.85
Aniline	30	30.6
Monomethylaniline	60	59.3
Dimethylaniline	10	10.2
Aniline	51.6	51.9
Monomethylaniline	14.82	15.05
Dimethylaniline	33.55	34.6
Aniline	57.7	58.0
Monomethylaniline	27.1	26.8
Dimethylaniline	15.2	16.1
Aniline	19.15	17.7
Monomethylaniline	55.4	56.9
Dimethylaniline	25.4	25.2
Aniline	32.9	33.3
Monomethylaniline	23.55	23.0
Dimethylaniline	43.6	43.7
Aniline	31.1	31.1
Monomethylaniline	16.95	16.72
Dimethylaniline	51.6	51.6
Aniline	22.35	23.2
Monomethylaniline	50.65	49.7
Dimethylaniline	26.92	26.4
Aniline	23.6	22.5
Monomethylaniline	14.7	15.9
Dimethylaniline	61.7	62.2
Aniline	20.5	20.1
Monomethylaniline	10.3	10.6
Dimethylaniline	69.3	69.0
Aniline	30.4	30.1
Monomethylaniline	23.2	23.6
Dimethylaniline	46.4	46.2

Mean square errors:

$\sigma_{aniline} = \mp 0.34$ ml, $\sigma_{monomethylaniline} = \mp 0.27$ ml, $\sigma_{dimethylaniline} = \mp 0.18$ ml, $\sigma_{diazotization} = \mp 0.12$ ml; $\sigma_{S_1} = \mp 0.23$ ml, $\sigma_{S_2} = \mp 0.4$ ml,

where $S_1 = 0.2$ N–A and $S_2 = 0.2$ N–C.

$$\sigma_{S_2} > \sigma_{S_1}.$$

2.55) containing the same amount of tropeoline 00 [18]. Instead of titrating with tropeoline 00, potentiometric titration of the solution to a pH of 2.55 can also be recommended. Let the amount of 0.5 N NaOH used be A ml (A should not be less than 5 ml).

If a hydrochloric aqueous solution of amines is being titrated, and not an anhydrous mixture, then after determination of excess acid, as just described, phenolphthalein solution is added and titration carried out with alkali to the color change. Additional expenditure of alkali with phenolphthalein should amount to 0.2 N−A ml.

3. Determination of nitrite used for diazotization of aniline and nitrosation of monomethylaniline is carried out by known methods [12, 13] on 50 ml of the solution prepared. Let the amount of 0.5 N nitrite solution used be B ml.

4. Determination of the amount of acid used up for diazotizing aniline. To 50 ml of the solution prepared is added about 2 g of sodium bromide, B ml of 0.5 N acid (the number of ml determined in 3), and then, with dropwise stirring, the same number B ml of 0.5 N nitrite. If (A−B) is greater than 5 ml, then there is no need to add acid. After two to three minutes, ice is added followed by about 20 g of chemically pure sodium chloride. The temperature drops rapidly to −5° to −7°. Ten drops of a 0.2% alcoholic solution of dimethyl yellow is added and the solution titrated with 0.5 N NaOH until the color changes from rose to yellow (without a reference solution). Let the amount of 0.5 N NaOH used be C ml.

Calculations:	Dimethylaniline content	(0.2−A−B)	60.5/d %
	Aniline content	(A+B−C)	46.5/d %
	Monomethylaniline content	(C−A)	50.35/d %

If, according to 4, B ml of 0.5 N acid was not added, then

Monomethylaniline content	(B+C−A)	50.35/d %
Aniline content	(A−C)	46.5/d %

Here, d is the weight of the test mixture.

The method was checked (see the table) on mixtures of aniline (setting point −6.1°), dimethylaniline (setting point −1.95°), and monomethylaniline, obtained by hydrolysis from benzosulfomethylaniline (m.p. 75-76°).

For high contents of dimethylaniline and for ratios of dimethylaniline to aniline in excess of 3:1, systematic errors arise from the expenditure of nitrite on nitrosation of the dimethylaniline. Nevertheless, as is shown in the table, the accuracy of an analysis of mixtures is sufficient for technical analyses. Potentiometric titration to the break on the titration curves showed that the error Δa, depending on the contents of the various amines, within the concentration limits set in the procedure, does not exceed 0.25 ml of 0.5 N alkali and 0.25 pH units.

SUMMARY

A fairly accurate and simple method has been developed for the analysis of mixtures of aniline, monomethylaniline, and dimethylaniline in aqueous solutions.

LITERATURE CITED

[1] N.N. Vorozhtsov, Fundamentals of the Synthesis of Intermediate Products and Dyes [in Russian] (Goskhimizdat, Moscow, 1950) pp. 313, 500, 542.

[2] R.N. Lastovskii and Yu.N. Vainshtein, Technical Analysis in the Production of Intermediate Products and Dyes [in Russian] (Goskhimizdat, Moscow, 1958) p. 240.

[3] N. Houben, Methods of Organic Chemistry 4 [in Russian] (Goskhimizdat, Moscow, 1949) p. 754.

[4] F. Reverdin and C. de la Harpe, Ber. 22, 1004 (1884).

[5] A. Nelyubina, Anilinokrasochnaya Prom. 3, 355 (1934).

[6] A. Nelyubina, Anilinokrasochnaya Prom. 4, 120 (1933).

[7] K.G. Mizuch and A.Ya. Savchenko, Prom. Organicheskoi Khim. 7, 24 (1940).

[8] A.P. Terent'ev, L.B. Kupletskaya, and É.V. Andreeva, Zhur. Obshchei Khim. 26, 881 (1956).•

[9] R. Shanti et al., Non-Aqueous Titration [in Russian] (Goskhimizdat, Moscow, 1958) pp. 68, 93, 102.

[10] J.S. Fritz, Analyt. Chem. 22, 578 (1950); 25, 750 (1953).

[11] G. Gal'pern and N. Bezinger, Zhur. Anal. Khim. 13, 603 (1958).•

[12] GOST 3719-47.

[13] TU MKhP 1771-48.

[14] A. Hantzsch, Ber. 32, 3633 (1899).

[15] A.A. Cherkasskii, Prom. Organicheskoi Khim. 5, 322 (1938).

[16] V.E. Rostovtsev, Prom. Organicheskoi Khim. 11, 37 (1939).

[17] L.V. Grachev, Zhur. Obshchei Khim. 16, 575 (1946); L.V. Grachev and Kirzner, Zhur. Obshchei Khim. 17, 2268 (1947).

[18] I.M. Kolthoff and V.A. Stenger, Volumetric Analysis [Russian translation] (Goskhimizdat, Moscow-Leningrad, 1952) vol. 2, p. 139.

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A MICROMETHOD FOR THE DETERMINATION OF SUGARS BY MEANS OF THE COPPER COMPOUND OF TRIHYDROXYGLUTARIC ACID

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Earlier we described a method for the determination of reducing sugars by means of the copper complex of trihydroxyglutaric acid [1], which has an important advantage over methods based on the use of Fehling solution, since a strict proportionality is observed between the amount of univalent copper formed and the sugar present. The method suggested permits determination of glucose, fructose, and maltose with a high degree of accuracy. We found that this method can be used for the determination of microamounts of various sugars: glucose, fructose, galactose, xylose, maltose, saccharose, and also of glucose and saccharose in each others presence. In this case, again there is observed a proportionality between the amount of the sugar and the volume of permanganate solution used up in the titration.

The method permits determination of reducing sugars in various organic substances, e.g., in fruit juice, with a high degree of accuracy.

As tests showed, there is no need to purify technical trihydroxyglutaric acid specially [1].

EXPERIMENTAL*

The following solutions were used for the microdetermination of reducing sugars [1].

Solution No. 1. 40 g $CuSO_4 \cdot 5H_2O$ was dissolved in water, and the volume of the solution made up to 1 liter.

Solution No. 2. 128 g of trihydroxyglutaric acid and 207 g of sodium hydroxide were dissolved in water and the volume of the solution made up to 1 liter.

Experimental procedure. By means of a micropipet, n ml of the solution of the sugar (containing 0.1-9 mg of sugar) and 3-n ml of water was introduced into a series of test tubes. To these test tubes were then added 3 ml of solution No. 1 and 3 ml of solution No. 2. The test tubes were immersed in boiling water for six minutes, after which they were cooled with water to room temperature. The liquid was poured through a glass filter and the precipitate of cuprous oxide washed 2-3 times with hot, freshly boiled water. After the Bunsen flask containing the wash liquors had been replaced by a clean, small flask, the cuprous oxide was dissolved in 3-5 ml of ferric alum solution (containing 86 g of $FeNH_4(SO_4)_2 \cdot 12H_2O$ and 108 ml of concentrated sulfuric acid per liter) and was transferred onto the filter. The test tube and the filter were rinsed 2-3 times with small portions of cold, freshly boiled water. The filtrate containing divalent iron was titrated in the flask serving as a receiver during the suction process, with 0.01-0.2 N potassium permanganate solution supplied from a microburet, until the color of the solution changed from green to a weak rose. The permanganate was standardized against a pure sugar (e.g., against chemically pure glucose).

When a series of experiments is carried out, the time taken to carry out an analysis is the same as for microdeterminations by the Bertrand method [2, 3]. The results obtained are given in the table.

*R.A. Batyr took part in the work.

Sugar	Expt. No.	Taken, mg, a	Found, mg, x_i	Found, mg (mean) $\bar{x}$	Dispersion s^2	Accuracy $t_{0,95} \cdot s_{\bar{x}}$	Probable relative error $\frac{s_{\bar{x}} \cdot t_{0,95}}{a} \cdot 100\%$
Glucose	1—9	1,00	0,996—1,004	1,002	$11 \cdot 10^{-6}$	0,0025	0,25
	10—18	3,00	2,990—3,012	3,002	$57 \cdot 10^{-6}$	0,0056	0,19
	19—27	6,00	5,991—6,008	5,999	$54 \cdot 10^{-6}$	0,0053	0,09
	28—36	9,00	8,976—9,012	8,995	$188 \cdot 10^{-6}$	0,0105	0,12
Fructose	1—9	3,00	2,993—3,009	3,003	$77 \cdot 10^{-6}$	0,0067	0,22
	10—18	6,00	5,995—6,019	6,005	$57 \cdot 10^{-6}$	0,0058	0,10
	19—27	9,00	8,980—9,997	8,992	$54 \cdot 10^{-6}$	0,0056	0,06
Galactose	1—9	3,00	2,991—3,006	3,001	$56 \cdot 10^{-6}$	0,0057	0,19
	10—18	6,00	5,998—6,012	6,006	$55 \cdot 10^{-6}$	0,0057	0,09
	19—27	9,00	8,989—9,003	8,995	$55 \cdot 10^{-6}$	0,0057	0,06
Xylose	1—9	3,00	2,992—3,005	3,001	$42 \cdot 10^{-6}$	0,0050	0,17
	10—18	6,00	5,998—6,012	6,003	$49 \cdot 10^{-6}$	0,0054	0,09
	19—27	9,00	8,989—9,003	8,997	$55 \cdot 10^{-6}$	0,0057	0,06
Maltose	1—9	3,00	2,982—3,002	2,998	$78 \cdot 10^{-6}$	0,0068	0,23
	10—18	6,00	5,984—6,026	6,003	$270 \cdot 10^{-6}$	0,0126	0,21
	19—27	9,00	8,986—9,007	8,993	$110 \cdot 10^{-6}$	0,0080	0,09
Saccharose*	1—9	3,00	2,995—3,008	3,002	$47 \cdot 10^{-6}$	0,0053	0,18
	10—18	6,00	5,992—6,005	6,001	$42 \cdot 10^{-6}$	0,0050	0,08
	19—27	9,00	8,989—9,001	8,993	$36 \cdot 10^{-6}$	0,0046	0,05

*The saccharose was hydrolyzed by adding 2.5 ml of 10% hydrochloric acid to 50 ml of test solution and the mixture heated on a boiling water bath for 30 minutes. After cooling, the volume of the solution was made up to 100 ml.

Determination of saccharose in the presence of glucose. Solutions of glucose and saccharose were prepared containing 2.00 mg of the sugars per ml. The factor for permanganate, determined from nine determinations, was 1.832 on a glucose basis, and 1.635 on a saccharose basis.

2.18 ml of permanganate was used for titrating a mixture of 2.00 ml of glucose solution and 1.00 ml of saccharose solution before hydrolysis, while 3.40-3.42 ml of permanganate was used for titrating the same mixture after hydrolysis. The amount of saccharose found was 1.995-2.028 mg (mean of 9 determinations 1.999 mg).

During titration of a mixture of 1.00 ml of glucose solution and 2.00 ml of saccharose solution, 3.974-4.006 mg was found (mean of nine determinations was 3.992 mg as against 4.00 mg actually taken).

Determination of reducing sugars in grape juice by the method of additions. 10.00 ml of "Semil'on" grape juice was diluted to 1 liter.

6.265-6.302 mg of reducing sugar, calculated in terms of glucose, was found in 3.00 ml of juice. 2.095 mg of sugar was found in 1 ml, this value was the mean of nine determinations.

6.155-6.191 mg of reducing sugar was found in a mixture of 2.00 ml of juice solution and 1.00 ml of glucose (containing 2.00 mg). After subtracting the glucose, it was found that 1 ml of juice contained 2.088 mg of sugar (mean of nine determinations).

6.081-6.117 mg of reducing sugar was found in a mixture of 1.00 ml of juice solution and 2.00 ml of glucose solution; on subtracting the glucose it was found that 1 ml of solution contained 2.085 mg of sugar (mean of nine determinations).

Determination of reducing sugars in apple juice by the method of additions. 20.00 ml of apple juice was diluted with water to 1 liter.

2.309-2.345 mg of sugar was found in 1.00 ml of the juice solution by direct determination; the mean of nine determinations was 2.337 mg.

To 1 ml of the juice solution was added 2.00 mg of glucose. The amount of reducing sugar found was 4.324-4.361 mg; accordingly, 1 ml of the juice contained 2.344 mg of sugar (mean of nine determinations).

To 1 ml of the juice solution was added 4.00 mg of glucose. 6.304-6.340 mg of reducing sugar was found; therefore, 1 ml of the juice solution contained 2.328 mg of sugar (mean of nine determinations).

It follows from these results that the micromethod suggested permits accurate determination of the content of reducing sugars in fruit juices.

SUMMARY

A new micromethod is suggested for the determination of sugars by means of the copper compound of trihydroxyglutaric acid. The advantage of this method is the strict proportionality between the amount of sugar and the volume of permanganate used up in titrating the univalent copper formed.

The method permits determination of glucose, fructose, galactose, xylose, maltose, and saccharose with a high degree of accuracy.

The micromethod can be used for the accurate and rapid determination of sugars in fruit juices.

LITERATURE CITED

[1] A.V. Ablov and D.G. Batyr, Zhur. Anal. Khim. 12, 749 (1957).*

[2] A.N. Belozerskii and N.I. Proskuryakov, Practical Textbook on the Biochemistry of Plants [in Russian] (Sovetskaya Nauka, Moscow, 1951) p. 17.

[3] A.I. Ermakov, V.V. Arasimovich, M.I. Smirnova-Ikonnikova, and I.K. Murri, Methods for the Biochemical Study of Plants [in Russian] (Sel'khozgiz, Moscow-Leningrad, 1952) p. 170.

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BRIEF COMMUNICATIONS

QUANTITATIVE DETERMINATION OF ZINC BY MEANS OF PRECIPITATION CHROMATOGRAPHY

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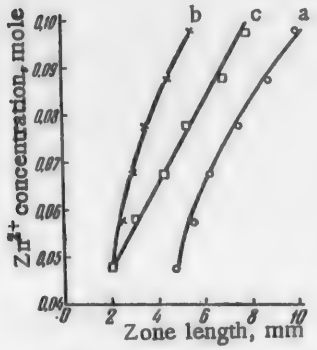
Precipitation chromatograms have clearly defined and even zone boundaries and an equal color intensity along the length of the zone. Under certain conditions, there is a definite relation between the length of the zone and the concentration of the material being chromatographed: the zone length expands with increasing concentration of the test material in solution [1, 2]. This made it possible to develop a method for the precipitation-chromatographic determination of the concentration of zinc ions in the form of its sulfide. Centrifuge tubes with a capacity of 10 ml and with a diameter of 12 mm at the cylindrical part were used for carrying out the precipitation-chromatographic experiments. All measurements were made in the upper, cylindrical part of the tubes. The carrier used was a 2% gel of agaroid [3] while the precipitant was sodium sulfide.



The relation between the zone length of ZnS and Zn^{2+} concentration: a) after separation of Zn^{2+} and Cr^{3+} in the course of 24 hours; b) after separation of $Zn^{2+}-Cr^{3+}-Hg^{2+}$ in the course of 15 hours; c) after separation of $Zn^{2+}-Cr^{3+}-Ag^{+}$ in the course of 24 hours.

As a result of preliminary experiments, it was established that the optimum ratio of carrier to precipitant is 5:2 (or 0.8 g of $Na_2S \cdot 9H_2O$ to 2 g of agaroid). (For this ratio the gel of agaroid has a pH of 10.)

The pH of the test solutions, as a rule, has no effect on the zone length.

0.5 ml or 1 ml of a solution with different concentrations of a zinc salt was placed on a prepared chromatographic column. It was established in the course of such experiments that the zone length increases linearly with increasing zinc-ion concentration of the solution [2]. However, it was also found that only 40% of the zinc, on an average, was precipitated from the solution in the gel.

Accordingly, in further experiments we tried to establish the conditions under which quantitative precipitation of zinc would be observed from the solution, while still maintaining the proportionality between the zone length and the concentration of zinc ions in solution. For this purpose, the effect of additions of solutions of chromium (III), mercury (II), silver, and lead (II) salts was studied, while the minimum zinc concentration which can still be determined with reasonable accuracy was also established. As a result of numerous experiments, the following technique was finally developed for the quantitative determination of zinc in the presence of chromium.

EXPERIMENTAL METHOD

A calibration curve was constructed by placing 0.5 ml (1 ml) of a zinc salt at various concentrations of 0.0476 M, 0.0576 M, 0.0676 M, 0.0776 M, 0.0876 M, 0.0976 M and 0.5 ml (1 ml) of 0.1 M $Cr_2(SO_4)_3$ on the agaroid gel containing the precipitant.

TABLE 1

Zone Length of ZnS for the Test Solutions

Solutions	Zn^{2+} concentration in solution, mole	Zone length, mm				
		1	2	3	4	mean
Known concentration (for constructing a calibration curve)	0,0976	10	10	—	—	10
	0,0876	8,5	9	—	—	8,75
	0,0776	7	8	—	—	7,5
	0,0676	6,5	6	—	—	6,25
	0,0576	5,5	5,5	—	—	5,5
	0,0476	4,5	5	—	—	5,75
Unknown concentration	X_1	8,5	8	8	8,5	8,25
	X_2	5,5	5	6	5,5	5,5
	X_3	7	7,5	7,5	7	7,25

Readings were taken after 24 hours. The chromium (III) zone was the same in all the tests (3.5 mm); the zones were clearly defined. The boundaries of the zinc zone were also sharp and even, the zone length being only dependent on the concentration. Qualitative reactions for zinc ions (in the solution above the gel) with dithizone and ammonium tetrathiocyanomercuriate gave negative results.

TABLE 2

Determination of Zinc Concentration by Titrimetric and Precipitation-Chromatographic Methods

Zn^{2+} solution	Zinc found, mole	
	by titration	by the precipitation-chromatographic method
X_1	0.0852	0.0845
X_2	0.0568	0.0575
X_3	0.0752	0.0760

Quantitative determination of zinc by the method indicated is possible for ratios of zinc and chromium (III), from equimolar solutions, equal to 1:1, 1:2, 1:10 by volume.

The curve relating the zone length to the zinc-ion concentration of the solution is shown in the diagram (a).

In order to check the method developed, zinc was determined in solutions in which its concentration was unknown; these were x_1, x_2, and x_3. The results are given in Table 1.

Using the results given in Table 1, a calibration curve was constructed, and this was used for establishing the zinc concentration of the test solutions: x_1, x_2, and x_3. The results obtained were controlled by titrimetric determination of the zinc with potassium ferrocyanide [4]. These results are given in Table 2.

During the quantitative determination of zinc in solutions of the ternary mixtures 1) $Zn^{2+}-Cr^{3+}-Hg^{2+}$; 2) $Zn^{2+}-Cr^{3+}-Ag^{+}$, thanks to the presence of the chromium, precipitation of zinc from solution proceeds quantitatively, while the relation between the length of the colored zone of ZnS and zinc concentration is also preserved. In these experiments again, to an agaroid gel containing Na_2S (in the proportion of 5:2) was added 0.5 ml (1 ml) of solutions of a zinc salt with the concentrations indicated above and 0.5 ml (1 ml) of a solution of 0.1 M $Cr(SO_4)_3$, and 0.5 ml (1 ml) of 0.1 M $AgNO_3$, or 0.5 ml (1 ml) of 0.1 M $Hg(NO_3)_2$. The relation between the zone length and the zinc concentration in the presence of the ions indicated is shown in the diagram (b,c).

SUMMARY

A quantitative precipitation-chromatographic method has been developed for the determination of zinc in the presence of trivalent chromium. The method is simple and requires only small amounts of test solution (0.5 to 1 ml).

The possibility has been demonstrated of determining zinc by the method indicated in solutions containing ternary mixtures: zinc-chromium-mercury and zinc-chromium-silver.

LITERATURE CITED

[1] K.M. Ol'shanova and V.D. Kopylova, Trudy Moscovskogo Tekhnologicheskogo Inst. Myasnoi i Molochnoi Prom. 5, 1955, pp. 54-62.

[2] M. Milone, G. Getini, and F. Ricca, Ann. Chem. 43, 10 (1953); Referat. Zhur. Khim. 11, 246 (1955).

[3] S.N. Stavros and A.A. Morozov, Ukrain. Khim. Zhur. 23, 721 (1957).

[4] V.I. Petrashen', Volumetric Analysis [in Russian] (Goskhimizdat, Moscow-Leningrad, 1946).

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DETERMINATION OF SMALL AMOUNTS OF BERYLLIUM BY MEANS OF β-DIKETONES

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Beryllium forms with β-diketones, acetylacetone derivatives, compounds which are very sparingly soluble in water [1]. It has been established that some of these diketones precipitate beryllium quantitatively. The present article contains a description of two methods for the gravimetric determination of beryllium by precipitating and weighing it in the form of its compounds with 2,2-dimethylhexanedione-3,5, $CH_3COOCH_2CO(CH_3)_3$ and 3-acetylhexanone-2, $CH_3COCH(C_3H_7)COCH_3$.

Saturated solutions of the diketones and a standard solution of beryllium sulfate with a concentration of 2 mg/ml Be were used for the work.

The method of precipitating beryllium with 2,2-dimethylhexanedione-3,5 consisted of the following. To the requisite amount of a saturated solution of the diketone, on the basis of 10-15 ml per mg of beryllium, pyridine was added until the pH was 5.5-6, and 0.2-0.3 ml of pyridine added in excess. The test solution of beryllium which had been diluted beforehand so that the beryllium concentration was 0.2-1.0 mg in 100 ml of solution was then added. After 5-10 seconds, a finely crystalline precipitate formed throughout the whole volume of the solution; after some time (1-1.5 hours), it collected in the form of coarse flocs on the bottom of the beaker, while the supernatant liquid became completely clear. The precipitate was then filtered through a No. 4 crucible and washed 4-5 times with distilled water; it was finally dried to constant weight at 50-55°.

Excess reagent does not interfere with the quantitative precipitation of beryllium; precipitation is better the lower the beryllium concentration of the solution.

TABLE 1

Precipitation of Beryllium with 2,2-Dimethylhexanedione-3,5

Be taken, mg	Precipitate obtained, mg	Be found, mg	Be taken, mg	Precipitate obtained, mg	Be found, mg
0,344	11,05	0,342	0,344	10,99	0,340
0,344	11,11	0,344	1,144	36,99	1,144
0,344	11,14	0,345	1,144	36,56	1,141
0,344	11,06	0,342	1,144	37,03	1,145
0,344	10,97	0,339	1,144	37,00	1,145

The concentration of the pyridine in the solution, which is necessary for establishing the requisite pH, did not usually exceed 0.5-0.7% by volume. Even a large excess of pyridine did not affect completeness of beryllium precipitation; however, too much pyridine in solution increases the time for the precipitate to coagulate. Ammonia solution cannot be recommended for adjusting the pH, since the results thereupon obtained are slightly low. This, apparently, can be explained by the low rate of formation of beryllium diketonate, as a result of which formation of the hydroxide occurs in parallel. Beryllium salts hydrolyze incompletely in the presence of pyridine, the hydroxide is not precipitated. Typical experimental results are given in Table 1.

*Deceased.

2,2-Dimethylhexanedione-3,5 is not a selective reagent for beryllium, although the stability of its complex compound with beryllium is considerably higher than, for example, the stability of its compound with aluminum. All those elements which, under the conditions used for precipitating beryllium, form sparingly soluble compounds with the β-diketone, will interfere with beryllium determination. Magnesium does not interfere, since it forms a diketonate at pH ≫ 9, i.e., after completion of the formation of the beryllium diketonate. Beryllium can be separated from magnesium by precipitating the former at pH < 9. Beryllium, in amounts of 0.1-0.3 mg, can be determined with a high degree of accuracy in the presence of 100 mg of magnesium.

The method of precipitating beryllium with 3-acetylhexanone-2 is the same as that for 2,2-dimethylhexanedione-3,5, with the exception that, for the precipitation of each mg of beryllium, less diketone solution is used (3-4 ml) because of the higher solubility of this diketone. In addition, ammonia can be used for adjusting the requisite pH in this case. The experimental results are given in Table 2.

TABLE 2

Precipitation of Beryllium with 3-Acetylhexanone-2

Be taken, mg	Precipitate obtained, mg	Be found, mg
2.183	70.7, 70.4, 70.5, 70.7	2.186, 2.181, 2.183, 2.186
0.229	7.35, 7.38, 7.36, 7.40	0.227, 0.228, 0.228, 0.229
0.114	3.74, 3.72, 3.70, 3.71	0.116, 0.115, 0.114, 0.115

The methods described can be recommended for the determination of small amounts of beryllium of the order of 0.1-3.0 mg in solutions of its pure salts, or after separation of beryllium in a pure state from impurities. Under such conditions, these methods have a number of advantages over other gravimetric methods for beryllium, e.g., over the methods in which beryllium is precipitated as its hydroxide or phosphate. The small conversion factor to beryllium of 0.03096 in both cases, the low hygroscopicity of the precipitate, and the low temperature at which it is dried to constant weight are points in favor of this form of weighing beryllium rather than the gravimetric form BeO. The crystalline nature of the precipitate and the constancy of its composition distinguish it from beryllium phosphate.

SUMMARY

Two methods are described for the determination of beryllium in which it is precipitated and weighed in the form of its compounds with 2,2-dimethylhexanedione-3,5 and 3-acetylhexanone-2.

LITERATURE CITED

[1] E.S. Przheval'skii and L.M. Moiseeva, Vestnik MGU, Seriya Matematiki, Mekhaniki, Astronomii, Fiziki, Khimii 1, 203 (1959).

[2] É.A. Ostroumov, New Methods of Chemical Analysis Using Organic Bases [in Russian] (Gosgeolizdat, Moscow, 1952).

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A PHOTOMETRIC PICRATE METHOD FOR THE DETERMINATION OF NAPHTHALENE IN ITS MIXTURES WITH PHENOL

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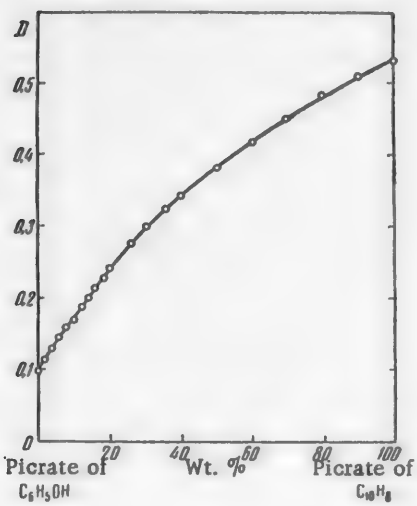
A spectrophotometric method of analyzing mixtures of phenol and naphthalene has been described in the literature [1]. As a consequence of the coincidence, in practice, of the characteristic frequencies in the absorption spectra of both components (273 and 275 mμ), the method presupposes the conversion of phenol into phenolate by the action of an alcoholic solution of alkali. The accuracy of this method, as the authors indicate, is about 4% [1].



We have developed a photometric method which is characterized by considerable simplicity and a high degree of accuracy. This method is the outcome of research carried out earlier [2], in which it was shown that, in the presence of aromatic hydrocarbons, the boundary of the absorption band of picric acid is shifted toward the long-wave part of the spectrum. The extent of this shift is determined by the character of the aromatic system and by the number of alkyl groups – substituents. During this work it was shown, for example, that the boundary of the absorption band of 0.1 M dichloroethane solutions of the picrates of benzene, its derivatives, and, in particular, of phenol is located in the region 412-425 mμ at an optical density of D = 1. Under the same conditions, the boundary of the absorption band of the picrates of naphthalene hydrocarbons is located at 455 mμ and higher. These solutions are characterized by a yellow color with varying intensity which means that it is possible to use a photometric method.

Weight % naphthalene	Optical density of solution of picrates, D	Naphthalene found, wt. %	Experimental error, %	Notes
7.6	0.149	6.9	−0.7	Melt
17.1	0.220	16.7	−0.4	Melt
22.3	0.250	21.5	−0.8	Mixture
22.4	0.248	21.2	−1.2	Melt
84.9	0.500	85.6	+0.7	Mixture

For this purpose, there is no need to use a quartz spectrophotometer; the determination can be carried out on any colorimeter – visual or photoelectric. We have carried out our work on an apparatus of the FÉK-M type using a blue light filter. The thickness of the absorbing layer is 20 mm.

Dichloroethane which had been washed several times with concentrated sulfuric acid until the latter ceased to acquire a color was used as the solvent. The dichloroethane was then carefully washed with water, dried with calcium chloride, and distilled [3].

EXPERIMENTAL METHOD

An aliquot of the test material (exactly 2 g) is dissolved in dichloroethane in a 100-ml standard flask; 5 ml of the solution obtained is mixed in the colorimeter cuvette with an equal volume of a standard solution of picric acid in dichloroethane, 100 ml of this solution contains 4 g of pure (recrystallized from alcohol) picric acid. Into a second cuvette, as a standard, is introduced 5 ml of the same solution of picric acid and an equal volume of pure solvent (in this way, the concentration of picric acid and of the picrates formed approximates to 0.1 M). The optical density of the test solution is measured and the naphthalene content corresponding to this optical density calculated from a calibration curve.

The calibration curve can be constructed with the aid of specially prepared mixtures of phenol and naphthalene, in which the weight of each mixture amounts to exactly 2 g. A curve of this type which we constructed is shown in the figure. Using this curve, we determined the naphthalene content of several of its mixtures or melts with phenol. The results obtained are given in the table.

The first part of the calibration curve (up to 20% by wt. of naphthalene) approximates to a straight line, as a result of which it is possible to establish the contents of the corresponding amounts of naphthalene not only graphically, but also by calculation:

$C = 140 (D - 0.099)$ wt. % of naphthalene; here, 0.099 is the optical density of the phenol picrate solution.

The accuracy of the suggested method is determined by the error in preparing the solutions. The solvent can be recovered from used solutions by a double distillation. The absence of traces of naphthalene or phenol in the recovered solvent should be checked by the technique described.

LITERATURE CITED

[1] S.G. Bogomolov, M.P. Grebenshchikova, and L.Ya. Liplavk, Materials of the Conference on Spectroscopy [in Russian] (Izd. Lvov Universiteta, 1957) p. 270.

[2] B.Ya. Teitel'baum and M.P. Dianov, Doklady Akad. Nauk SSSR 128, 106 (1959).*

[3] A.Ya. Berlin, Laboratory Technics in Organic Chemistry [in Russian] (Goskhimizdat, Moscow-Leningrad, 1952).

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THE GLASS PARTS OF POLAROGRAPHIC APPARATUS

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The glass parts of polarographic apparatus – cells, capillaries, etc. – supplied with commercially available polarographs are not suitable enough. Even such an advanced apparatus as the Énergochermet TsLA recording polarograph [1] is provided with a cell with an internal (not isolated from the test solution) anode which does not have a jacket for thermostatting the apparatus. The capillaries supplied with this polarograph for the dropping electrodes do not enable one to use the apparatus to its best advantage. Actually, the large dropping period of these electrodes compels one to damp the apparatus; this leads to a sharp increase in the inertia of the following system and to considerable distortion of the shape of the polarographic curves. This had led us to publish details of a considerably more convenient, in our opinion, design for the glass parts of the polarograph, a design which has been used in our Institute for several years.

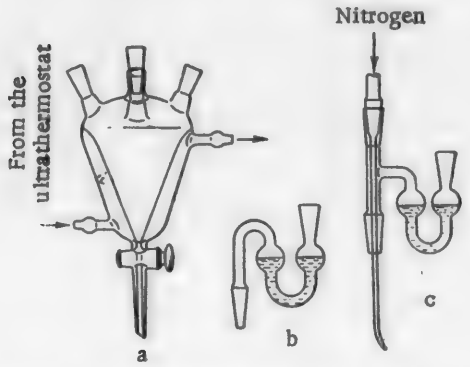

Fig. 1. Polarographic cell (a) and water seals (b and c).

Fig. 2. The method used for fusing the blade onto the capillary tip.

The cell (Fig. 1a) is a conical vessel with a jacket which can be thermostatted by means of an ultrathermostat of the Heppler type or the TS-15 type. The lower, narrower end of the cell is provided with a tap for running off mercury or solution; the upper part of the cell has five inlets with normal ground-glass joints (NSh 10). The central inlet is for introducing the capillary of the dropping electrode, the two side inlets for the anode, and the reference electrode, the other for a capillary through which nitrogen is supplied, and, finally, the last inlet is used for introducing the test solutions, and is usually sealed with a water-seal (Fig. 1b), through which the nitrogen escapes to the atmosphere.

Sometimes – with the aim of freeing one inlet, e.g., for connecting a buret so that there is no access to atmospheric oxygen – it is necessary to connect the inlet and outlet for the nitrogen into one. In such a case, the capillary for the nitrogen is placed in the cell through a socket provided with a water seal (Fig. 1c). The cell is supported on a stand by placing it in a rubber ring stretched over a metal ring, a small piece of the latter being sawed out so that it is possible to slip the rubber tubing over it. In order to fix the cell firmly in position, a rubber bung is fitted onto the stem of the cell, and this bung is clamped in a boss and clamp-fitted to the same stand.

Dropping electrode. The most convenient type of electrode, both for analytical and research purposes, is a dropping electrode in which the drop is forced to drop off by coming into contact with a small blade [2]. The capillary of the electrode is prepared by drawing out a thermometer tube so that the length of the working (narrow) part amounts to 40-80 mm, while the diameter of the canal is 30-60 μ. The blade is fused on as follows. Air or nitrogen is passed continuously through the canal. The capillary tip, that part to which the blade is to be fused, is introduced into the small sharp flame of a blowpipe; simultaneously, into the flame is introduced a capillary tube of the same glass, drawn out beforehand into a thread (diameter about 0.1 mm) (Fig. 2a). As the thread

Fig. 3. Supply reservoir of mercury.

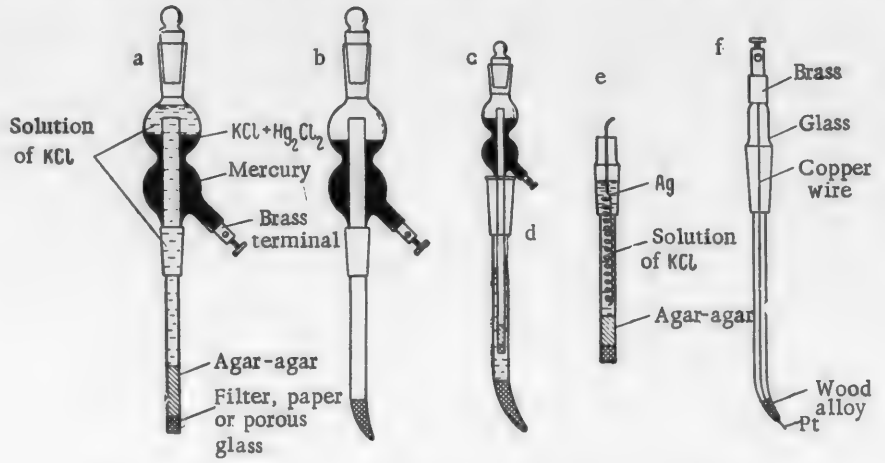

Fig. 4. Nonpolarizable electrodes and intermediate salt bridges.

softens (its tip starts to thicken) its tip is allowed to touch the heated cylindrical part of the capillary right at its end; the thread then sticks to the capillary. Without withdrawing the joint from the flame, the thread is bent; it is then drawn out, and finally fused (Fig. 2). By placing the blade in the flame it is thickened, and by means of a tungsten needle it is arranged that there is a gap of 0.5-1.5 mm (depending on size of drop required) between the blade and the mouth of the capillary. The core of a normal No. 10 ground-glass joint is fitted to the top of the capillary, the upper end of the joint being connected to a supply reservoir of mercury (Fig. 3); it is best that this reservoir should be provided with a tap.

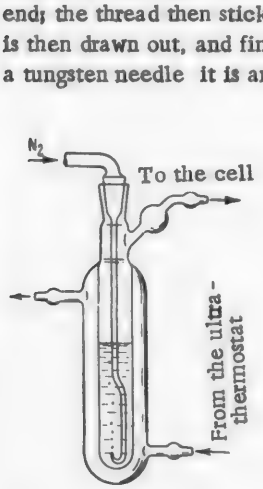

Fig. 5. Vessel for saturating the nitrogen with solvent vapor.

Nonpolarizable electrodes. As external anodes and reference electrodes, it is most convenient to use calomel electrodes, similar in form to electrodes prepared by the "Moskip" factory for the P-4 potentiometer (Fig. 4). Contact with the mercury is effected through a platinum wire fused into the glass; the wire is connected on the outside to a brass terminal (Fig. 4a), which is fused to the glass. The tip of the electrode siphon is sealed with a tightly rolled piece of filter paper and is filled with agar-agar gel and potassium chloride. In the reference electrodes the siphon is drawn out into a capillary, the end of which is placed close to the dropping electrode during measurements (Fig. 4b). On top, in the wide part of the electrode, calomel and KCl crystals are placed on top of the mercury. When it is desirable that the test solution should be free from chloride ions (e.g., when polarograms are taken at potentials more positive than that of the calomel electrode [3]) or potassium ions (when work is being carried out in the strongly negative potential region), then the nonpolarizable electrode is filled with mercury sulfate and potassium sulfate [3] or with tetrasubstituted ammonium salts. For potentiometric measurement of the potential of the dropping electrode with respect to the calomel electrode, or during work in such solutions, it is expedient to have a special calomel electrode with a narrow siphon (Fig. 4c), which is not placed directly in the cell, but through an intermediate salt bridge (Fig. 4d) of agar-agar, containing potassium sulfate (or nitrate) or tetrasubstituted ammonium salts, respectively. A bridge of this type can be used for preparing an external silver chloride electrode. For this purpose, a silver spiral or foil is inserted into it and the bridge filled with a potassium chloride solution (Fig. 4e).

When it is desirable to use a mercury pool as the nonpolarizable electrode, then a special electrode (Fig. 4f) is inserted into the cell instead of the external electrode, in order to establish contact with the mercury pool.

Vessel for saturating nitrogen with solvent vapor. Before the nitrogen is passed into the cell, it is necessary to saturate it with the vapors of the solvent used in the test solution at the experimental temperature. The vessel shown in Fig. 5 is suitable for this purpose. The nitrogen is bubbled through the solvent which is kept at the same temperature as the test solution. The jacket of the vessel is connected in series with the cell jacket, so that the vessel and cell are both thermostatted by means of the same ultrathermostat.

LITERATURE CITED

[1] S.B. Tsfasman, Zavodskaya Lab. 22, 131 (1956).

[2] E.M. Skobets and N.S. Kavetskii, Zavodskaya Lab. 15, 1299 (1949).

[3] S.G. Mairanovskii, A.A. Fainzil'berg, S.S. Novikov, and V.A. Klimova, Doklady Akad. Nauk SSSR 125, 351 (1959).*

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*Original Russian pagination. See C.B. translation.

SOME IMPROVEMENTS IN THE MICROCRYSTALLOSCOPIC DETECTION OF POTASSIUM AS THE TRIPLE SALT POTASSIUM, COPPER, AND LEAD NITRITE

A.V. Pavlinova, M.V. Korotun, and A.E. Protsenko

Chernovitskii State University

Microcrystalloscopic detection of potassium on the basis of the formation of black cubes by the action of a solution of $Na_2CuPb(NO_2)_6$ permits detection of 0.15 γ K at a limiting dilution of 1:6600 [1]. The recommended procedure for preparing the reagent is to take 20 g of $NaNO_2$, 9.1 g of $Cu(CH_3COO)_2$, and 1.6 g of $Pb(CH_3COO)_2$ in 150 ml of distilled water acidified with 2 ml of 30% CH_3COOH. We tried to increase the sensitivity of detection, and to accelerate formation of crystals of $K_2CuPb(NO_2)_6$, by increasing the concentration of $Pb(CH_3COO)_2$ or $NaNO_2$ in the reagent. Solutions of the reagent, and of KCl of decreasing concentration, were placed dropwise on a glazed porcelain plate and the rate with which the crystals formed observed visually.

Tests showed that the $NaNO_2$ concentration, as one would expect, has a strong effect on the rate at which a precipitate appears, and on the sensitivity of potassium detection.

On using a reagent containing 25 g of lead acetate, 6.0 g of copper acetate, and 40 g of sodium nitrite, the limit of identification of potassium proved to be 0.9 γ K, when the reaction was carried out in a test tube, the limiting dilution being 1:1026. For microcrystalloscopic detection of potassium, a drop of the test solution was evaporated to dryness on a glass plate, after which a drop of reagent solution was added. The appearance of the characteristic crystals was observed at a potassium chloride concentration as low as 0.0025 M. The limit of detection was 0.9 γ K, while the limiting dilution was 1:10,300.

SUMMARY

By increasing the concentration of $NaNO_2$ and $Pb(CH_3COO)_2$ in the reagent used for detecting potassium [$NaNO_2$, $Pb(CH_3COO)_2$, and $Cu(CH_3COO)_2$], it is possible to increase the sensitivity of the microcrystalloscopic detection of potassium to 0.9 γ K; the limiting dilution is 1:10,310.

LITERATURE CITED

[1] L.M. Korenman, Microcrystalloscopy [in Russian] (Goskhimizdat, Moscow, 1955) pp. 118, 350.

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ALEKSANDR MAKSIMOVICH DYMOV

(ON HIS 60TH BIRTHDAY)

One of the directions taken by the scientific-technical activity of A.M. Dymov, particularly in the initial period, was the development of analytical methods for original raw materials, slags, and the finished articles of ferrous metallurgy, with their subsequent unification (standardization); this was the result of the acute demands of industrial chemical laboratories for such methods in connection with the restoration and development of Russian metallurgy and machine construction. As a result of this work, the Commission of the Soviet of industrial laboratories issued several collections of industrial methods of analysis (Chemical Analysis of Carbon and Alloy Steels, Cast Iron, and Ferroalloys, 1937; Standard Methods of Analyzing Cast and Steel, 1940; Collected Methods of Analysis of Cast Iron and Steel, 1944); the three were issued under the joint editorship of Academician É.V. Britske and A.M. Dymov. These collections proved of considerable help to industrial laboratories and to the development and improvement of the analytical chemical control of the metallurgical and machine construction industries.

In recent years (1953-1958), in the same field, A.M. Dymov has participated in developing international standards for analytical methods for manganese ores (he has been in charge of the work of the Soviet delegation of analysts at two international conferences in 1954 and 1956 which examined these standards).

In connection with the work on the standardization of analytical methods, together with his direct participation in their experimental development, A.M. Dymov compiled "Tables of Permissible Deviations in Experimental Results" for the appropriate elements, and has published a series of articles on the accuracy of chemical analytical methods which are applied to the control of metallurgical production, and for developing standard samples (standards) for increasing the quality (accuracy) of such control (the articles "The Accuracy of Methods of Analytical Control," 1937 and 1938; "Standard Samples and Their Part in Production Control," 1952).

A.M. Dymov's direct connection with industrial laboratories and his knowledge of their current demands are reflected in his published work. Thus, the books "Industrial Methods of Metallurgical Analysis, Rapid and Arbitrary," 1933, and "Technical Analysis of Ores and Metals" (which has reached five editions) have received wide recognition in industrial and scientific-research laboratories (the second book, which covers 50 pages, is a bench textbook in industrial and research laboratories; it has been translated into Chinese and Rumanian, and has been awarded a Stalin prize).

A.M. Dymov has paid special attention to the development of rapid (express) methods of analysis, the need for which has arisen from, and is arising from, improvements in technological processes (their intensification) in metallurgy and machine construction.

A.M. Dymov has developed and published several methods of this type ("A Rapid Method for the Determination of Silicic Acid in Alunites," 1930; "A Rapid Method for the Determination of Manganese in Bronzes," 1936; "Rapid Analysis of Ferrosilicon," 1937; "A Rapid Semimicro Method for the Determination of Calcium Oxide in Slags," 1946).

A.M. Dymov has also been interested in the questions of organizing industrial laboratories and in setting up chemical control of metallurgical production. He was a member of the technical commission set up by the chemical laboratories of the Magnitogorsk Metallurgical Combine, and of a commission for checking accepted methods of analysis, in connection with the starting of the first blast furnace (1931-1932). He published a number of articles on these questions including "A Giant of Socialist Industry – A Powerful Laboratory Base," 1932; "Laboratories for Industrial Enterprises," (in the paper "Izvestiya" 2, 1932); "The Role of the Central Industrial Laboratory," (in the paper "Tekhnika," 1932), and also articles devoted to experiments carried out abroad on the organization of industrial laboratories, and on accepted analytical methods (the article "Setting Up Production Control in German Industrial Laboratories," 1933, etc.).

At the first All-Union conference on analytical chemistry (1939) he read and published a report on the theme "The State and Organization of Analytical Control in Ferrous Metallurgy."

Another question which drew A.M. Dymov's attention was the training of qualified cadres of analysts, a question which hardly received any attention in pre-revolutionary Russia; he published a series of articles on this subject "Cadres of Analysts for Industrial Laboratories," 1954; "The Training of Personnel for Industrial Laboratories," 1938, etc. A.M. Dymov took part in organizing courses for training and improving the qualifications of analysts.

The articles "Industrial Laboratories in Capitalist Russia and Under the Soviet Government," and "Progress in Analytical Chemistry in the USSR in 40 Years," reflect the development of our industrial laboratories attached to the metallurgical and machine-constructing industries, and of analytical methods of control.

A.M. Dymov has developed physicochemical methods as well as classical methods and has introduced them into scientific-research work, and applied them to daily practice in industrial laboratories. He (together with co-workers) has developed and published a number of photocolorimetric methods for determining elements in iron alloys (nickel, cobalt, silicon, tungsten, lead); he has also published a polarographic method for determining iron, etc.

In recent years, A.M. Dymov and his co-workers have been developing methods for the determination of small amounts of elements and microimpurities in technical and pure metals. Mention may be made of the methods developed for the determination of low magnesium contents in modified casts and in metallic nickel of high purity, of arsenic and copper in metallic molybdenum, of magnesium, tungsten, and chlorine in metallic titanium, and of aluminum in carbon steels.

Several of the investigations he has carried out on developing analytical methods have been checked with the aid of radioactive isotopes (for example, the methods of determining phosphorus in ferroniobium and ferrotitanium).

It should be noted that the sequence in which A.M. Dymov developed methods for the determination of the components of iron and other alloys corresponds to the development of Russian metallurgy and machine construction in relation to the production of new brands of alloyed steel, ferroalloys, and the production of pure metals.

A.M. Dymov has written several textbooks. As long ago as 1929, he published A Textbook of Laboratory Technical Analysis, which went to five editions; in conjunction with members of the chair of analytical chemistry of the Moscow Steel Institute, he published a number of laboratory textbooks on quantitative analysis by a semi-micro method. In 1959, A.M. Dymov published a textbook on the analysis of metallurgical slags, and is now preparing a textbook on the analysis of iron and manganese ores.

Mention must also be made of the large amount of work he has carried out in editing and reviewing textbooks and journals in the field of analytical chemistry and technical analysis.

A.M. Dymov is a member of the editorial board of the Journal of Analytical Chemistry USSR, and of Industrial Laboratories.

The Commission on Analytical Chemistry and the Editorial Board of the Journal of Analytical Chemistry, Academy of Sciences, USSR, wish A.M. Dymov many years of fruitful scientific work and success in educating the young generation for the good of our country.

CHRONICLE

PROGRESS IN ANALYTICAL CHEMISTRY IN CHINA

D.I. Ryabchikov

In 1952, a vast network of analytical laboratories was established in China in the specialized, reopened Institutes of the Academy of Sciences and Ministries and their branches in the provinces (in the chemical faculties), in the places of work of geological prospecting parties, and, later, even in the social communes. The chemical methods predominantly used initially for production control have, in recent years, been replaced by more accurate and rapid instrumental methods. Equipment is designed for small laboratory groups working on the analysis of mineral wealth. Massive preparations are being made for field laboratories.

During the development of enrichment schemes, and then for the technological treatment of the raw material, particularly for the production of nonferrous and rare metals, analytical control is used to a considerable extent. As a rule, all new industrial enterprises are provided with good analytical laboratories.

The importance of the analytical control of production and the quality of the finished products in all branches of industry and agriculture were clearly demonstrated in the All-Chinese Exhibition of Industry and Transport held in Peking toward the end of 1958, and in the Agricultural Exhibition held in January, 1959. At these exhibitions, there were shown examples of modern Chinese laboratory apparatus including: high-quality analytical balances, photocolorimeters, polarographs, spectrographs, various electrical heating equipment, glass and porcelain vessels, and a very large variety of reagents (up to 5000 items). All this has been produced on the bases of reconstructed industrial enterprises and experimental shops in scientific-research institutes and colleges.

The wide scope of analytical work in the country has demanded that the problem of cadres of workers be solved. Few analysts were trained in the small number of colleges of old China. In 1952, during the reforms that were carried out in the chemistry faculties of the universities, chairs of analytical chemistry were created. Training of analysts is now carried out in China in universities and in specially created educational establishments, at intermediate and higher levels, in chemical, geological, and metallurgical institutes of the Academy of Sciences. More and more analytical work is being started in the chairs of analytical chemistry and in the analytical laboratories of the chemical institutes of the Academy of Sciences. Of interest is the methodical work on developing simplified methods for the analysis of soils, fertilizers, cast, steel, copper, etc., for social commune laboratories.

The teaching laboratories of the chemistry faculties are well provided with the requisite equipment, apparatus, and reagents. The faculty libraries and the libraries of scientific-research institutes are well stocked with literature. Many Russian textbooks have been translated into Chinese. Fundamental foreign textbooks are photocopied after 2-3 months and pass into the country's libraries.

In connection with the development of new technics, methods have been developed and adopted for the determination of trace impurities in specially pure metals and compounds.

The classical methods of precipitation, coprecipitation, and the separation of the elements have been further developed in order to apply them to the concentration and determination of traces of inorganic components in the work carried out by En Jeng-ying (Peking University), Liang Shu-ch'uan (Institute of Chemistry of the Academy of Sciences), and Shu-shang (Institute of Applied Chemistry of the Academy of Sciences). Work has also started along the same directions on microchemical methods of analysis by Chung Yu-lan (Institute of Chemistry of the Academy of Sciences).

Ts'on Yung-hua at the Institute of Applied Chemistry of the Academy of Sciences, organized a group for carrying out polarographic analysis in Changchung; subsequently, soon after the liberation, Liu Ch'en-i carried on

with this development, and three years afterward, the method became widely used in the country. Kao Siao-hsa carries out research on the theory of the polarographic method in Peking University. In recent years, work has started on oscillographic polarography. Work is being carried on in a number of institutes on developing new marks of polarographs. The chromatographic method has been widely used in recent years for separating complex mixtures, and for preparing the rare and rare-earth elements in pure form. Of special interest in this connection is the work directed by Ts'ung Huang-peng at the Institute of Applied Chemistry in Hangkung, and by Liu Ta-kang in the Chemical Institute in Peking. Success is being achieved in synthesizing ion-exchange resins, particularly in the chemical institutes and in the Institute of Applied Chemistry of the Academy of Sciences. Chromatography and electrochromatography on papers is being successfully carried out for the analysis of the rare earths, while, in Shanminsk University, Lu Ts'un lan and Huang Yu-ying have determined microamounts of the alkali metals by this method.

Spectrographic methods of analysis are particularly widely used in connection with the express analysis of steel and nonferrous metals. Research on spectroscopy is carried out at the Institute of Applied Chemistry of the Academy of Sciences in Changchung under the guidance of Hsueh-chou.

There are well-equipped laboratories for spectrographic analysis in a number of the institutes of the Academy of Sciences (the Institute of Geology and Chemistry in Peking; the Institute of Metallurgy and Ceramics in Shanghai; the Institute of Mining and Metallurgy in Chansha, and other institutes), in many other institutes, universities, and factories. Initially, the requisite apparatus was imported from the Soviet Union, the German Democratic Republic, and England; in recent years, however, production of spectrographs has been organized in China on the basis of models developed in the Institute of Optical Glass in Changchung.

In a short time, analytical chemistry has assumed in China an important part in solving practical problems in the most diverse branches of science and technics. A sound technical material basis has been developed, many analysts have been trained, and, with the interest shown by the Communist Party and the Chinese Government, analytical chemists are honorably struggling with the huge problems posed by the second five-year plan for the development of the social economy of China.

A NEW REAGENT FOR THE DETERMINATION OF SCANDIUM AND VANADIUM – "SULFONAZO"

A new reagent which has been designated "sulfonazo" has been synthesized at the All-Union Scientific-Research Institute of Chemical Reagents (IREA) for the photometric determination of scandium and vanadium.

The new reagent possesses several advantages over the reagents widely used at present for these cations; it is characterized by its high sensitivity and selectivity, and by the stability of the colored solutions it forms.

Organizations and enterprises who would like to test the new reagent may receive a free sample and instructions for its use on applying to the address of the Institute of Chemical Reagents (Moskva, Zh 33, Samokatnaya Ul; D.4a), so that they can, within two months of receiving the sample, report back to the Institute on the practical value of the reagent.

The Institute is willing to advise on all questions relating to the use of "sulfonazo."

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

HIGH TEMPERATURE CHEMISTRY OF SILICATES AND OTHER OXIDE SYSTEMS

By N. A. Toropov and V. P. Barzakovskii

I. V. Grebenschikov Institute of Silicate Chemistry, Academy of Sciences of the USSR

Translated from Russian by **C. N. Turton** and **T. I. Turton**

A review of important work done on the high-temperature behavior, properties, and phase diagrams of systems of two or more oxides, especially where one of the oxides is silica, including pyrocerams, spinels, cordierite, and various ferrites. Investigative methods are described and methods of determining thermodynamic properties are examined. A Special Research Report.

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